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# STUDIES IN ALUMINA AND ALUMINIUM PRODUCTION

## MODEL LABORATORIES FOR TESTING BAUXITE, ALUMINA AND INTERMEDIATE PRODUCTS IN DEVELOPING COUNTRIES

id.73-1741

## EXPLANATORY NOTES

Reference to "tons" indicates metric tons.

The following abbreviations have been used in this document:

Å = Angström

ml = millilitre

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The views and opinions expressed in this study are those of the consultant and do not necessarily reflect the views of the secretariat of UNIDO.

# PREFACE

In response to a recommendation of the Expert Consultative Group on the Alumina Industry, which met in Vienna in 1967, the United Nations Industrial Development Organization arranged for the preparation and distribution of a series of four studies[1] on some of the more important aspects of bauxite mining, alumina and aluminium production marketing and fields of application of aluminium, especially as they affect the developing countries.

In the present study, the third in the series, K. Sólymár Research Institute for Non-Ferrous Metals, Budapest, Hungary considers in detail the requirements for establishing bauxite-testing laboratories of three different kinds: a field service laboratory for use by prospecting teams or at mining operations; a laboratory for the chemical and technological examination of bauxites; and a central laboratory for advanced alumina technology that would be associated with an institution of higher education. Very detailed specifications are given for each of these three installations, together with descriptions of the kinds of analytical and technological testing that they may be called upon to perform. Two annexes deal with the scientific basis for phase analysis of bauxite and red muds and the formulation of bauxite digestion curves.

In the first of these four studies, G. Dobos, Managing Director of the Hungarian Aluminium Trust, considers the implications of the fact that it is becoming increasingly necessary to use bauxitic raw materials that were formerly considered non-economic and that are unsuitable for the conventional Bayer process. The qualities of bauxites for use in the Bayer process are also considered in detail.

In the second study in the series, Rajindra Manocha (Società Alluminio Veneto p.A., Venice, Italy) describes the analytical and technological information required by the alumina industry and the testing methods available for obtaining it. The requirements for alumina laboratories of three specialised kinds are considered in detail. This study may be considered as being complementary to the present one.

In the fourth and final study in the series, Samuel Moment, an American consulting industrial economist, reviews the present state and anticipated

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[1] See UNIDO/ITD.170, UNIDO/ITD.171, UNIDO/ITD.172 and UNIDO/ITD.173.

development of the world primary aluminium industry, with special reference to some of the countries of the Pacific basin. It concludes with an appraisal of the possibilities for expanding aluminium production in some of the countries that are members of the Economic Commission for Asia and the Far East (ECAFE).

By issuing these studies, UNIDO hopes to make a practical and significant contribution to the dissemination of information and also to the creation and transfer of sources of specific know-how for developing countries in this important industrial field.

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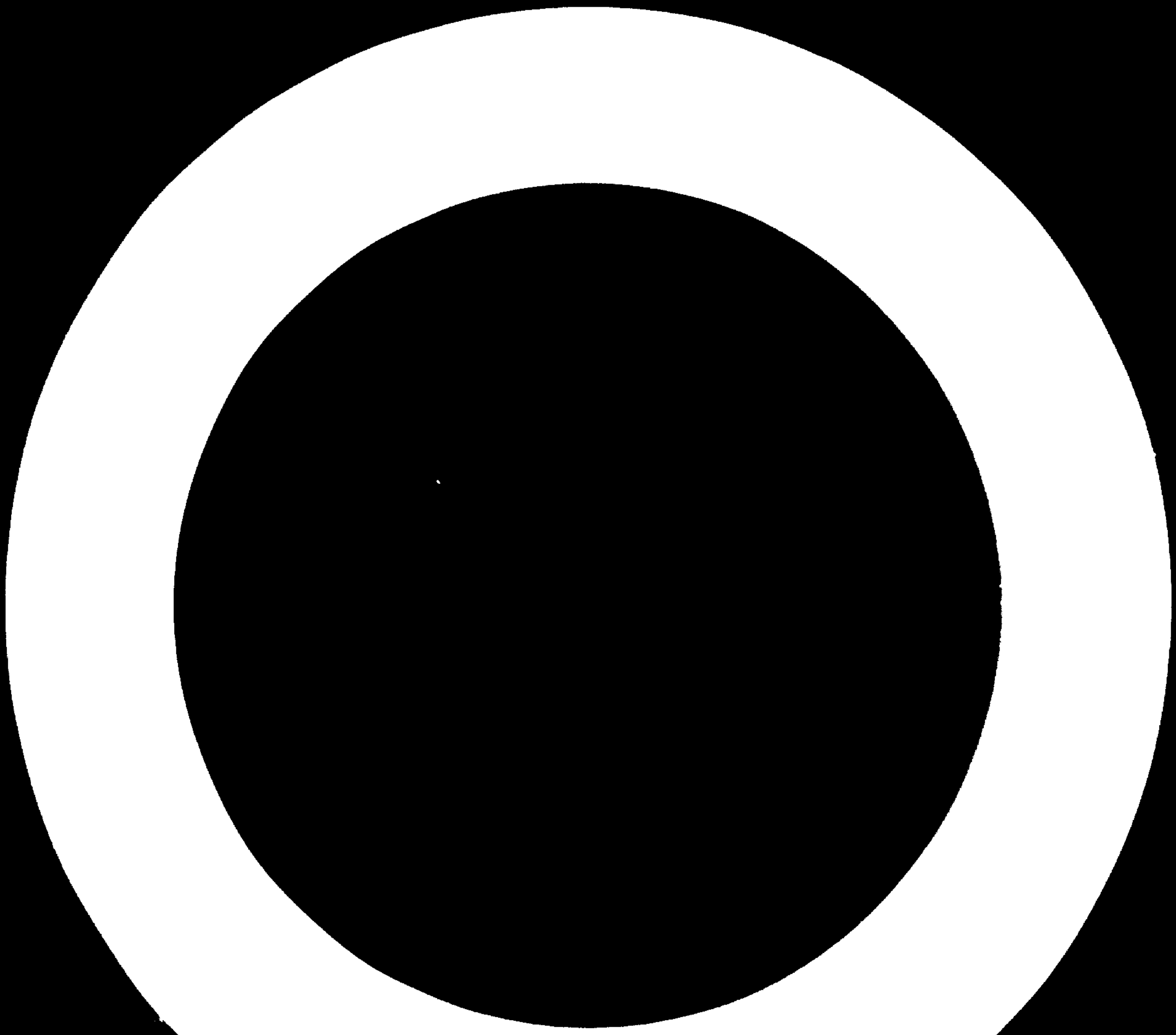


# INTRODUCTION

About [illegible] per cent of the world's bauxite reserves are located in the developing countries, while over [illegible] per cent of the world's aluminium production is supplied by the developed ones. The world's potential bauxite resources, which are estimated to be [illegible] billion [illegible], are also located mainly in Asia and Africa [1]. There is thus every reason why the properties of the bauxite deposits in the developing countries should be thoroughly understood.

The present report covers the activities that must be carried out in bauxite testing laboratories, outlines modern testing methods and describes three types of model laboratory, which serve different purposes and cost different amounts. The design of these laboratories is modular, so that, by the addition of further items of equipment, the simplest type can be developed easily into a more advanced one.

The most important tests that have to be carried out in these laboratories and the equipment required for them are discussed in detail, and a full list of bibliographical references is provided. In addition, the personnel required and their qualifications are listed and recommendations about their training are made. Two annexes give detailed descriptions of phase analysis and laboratory-scale technological tests for bauxite, with some examples.

Model laboratories can be built near bauxite deposits or connected with alumina plants, either as independent research centres or as parts of existing research institutes, universities or other institutions. The latter form of organization has the advantages that expensive equipment and instruments can be utilized to a greater extent, and the laboratory can fulfil an educational function in training staff members for alumina plants. For these reasons, local conditions and possibilities for further development should be considered carefully when the decision about the location of the plant is taken. The primary aim of this report is to promote bauxite testing in developing countries. However, it should be added that the model laboratories recommended are also suitable for more developed industrial countries that possess bauxite resources.

## Installation of model laboratories

When relating investment to the capabilities of the three types of laboratories discussed here, model laboratories types 1 and 2 (with some modifications) can be recommended generally. Model laboratory type 3 can be recommended for research centres that will form part of future alumina plants or be in association with existing university facilities. Model laboratories of both type 2 and type 3 are equipped to perform the educational function of training staff for alumina plants.

If a decision is taken, detailed project plans and cost calculations must be prepared for the model laboratories. When the test programme has been approved, detailed instructions and specifications must be prepared for all operations.

## Orders for projects, preparation of work instructions, and training of personnel

Chiefly because there is very little literature available on specific experience and detailed techniques for bauxite analysis and technological evaluation, it would seem desirable to make one organization responsible for all tasks connected with setting up model laboratories, namely the preparation of detailed projects and cost calculations, the preparation of work instructions and the training of personnel.

# THE FUNCTIONS OF MODEL LABORATORIES

Before the detailed descriptions, a brief survey is given of the role and functions of the laboratories, starting with the simplest.

Model laboratory type 1 is a service laboratory for the geological exploration of bauxite deposits and for use at bauxite mines. It is the simplest of the three types discussed and performs the analyses called for by bauxite exploration and mining. It can be located on site or can form part of an existing laboratory or educational establishment.

The role of this type of laboratory is usually restricted to the determination of the five major constituents of bauxite, as defined by international practice - loss on ignition (LOI), alumina ($Al_2O_3$), silica ($SiO_2$), iron oxide ($Fe_2O_3$) and titaniumoxide ($TiO_2$), using wet analytical procedures. This type of laboratory fully satisfies the requirements if the bauxites to be tested all belong to the same type and do not vary widely in composition. The range of operations of the laboratory can, in due course, be extended to cover simple investigations of mineralogical compositions and digestibility (i.e. $Al_2O_3$ solubility in alkalis under specific process conditions, expressed as a percentage of the total $Al_2O_3$ content).

An expert would be required for the starting up period of the laboratory, but subsequently it would work independently. From time to time it would be advisable to make use of the facilities of external laboratories (for example, the laboratories of the large alumina-producing companies) in order to evaluate the technological value of the bauxites.

Model laboratory type 2 is designed for the chemical and technological evaluation of bauxites. In addition to performing all the functions of model laboratory type 1, the chemical analyses performed in this laboratory include determination of the impurities in bauxite that are important from the process point of view (i.e. carbonates, sulphates, pyrite, CaO, MgO, $P_2O_5$, $V_2O_5$, fluorine and organic matter) and the analysis of aluminate liquor and red mud. Technological tests are also performed that are designed to evaluate the bauxite in question in relation to the Bayer process. These tests are primarily digestion tests and settling tests on red mud. This type of laboratory is intended for testing bauxites that vary considerably in type and composition, since the tests mentioned allow the effect of quality variations on practice to be followed.

The laboratory may be set up independently or associated with an alumina plant, or it may also form part of an existing educational establishment or chemical laboratory. It is suitable for training personnel for alumina plants. If the laboratory is installed at such a plant, it should be equipped to perform all the analytical tasks associated with the Bayer process, such as analyses of bauxite and red mud slurries aluminate liquor, impurities in alumina, vanadium salt and soda salt.

Model laboratory type 3 is a complete research laboratory for bauxite testing and alumina technology and is capable of performing all the testing and research tasks connected with the alumina industry.

In addition to the functions of model laboratory type 2, its work includes the analysis of trace elements in bauxites, complete phase analysis of bauxites and red mud, and technological evaluation of various types of bauxite. The laboratory is equipped with high-performance instruments. It can be organized as an independent research centre or associated with an alumina plant. The inclusion of this type of advanced laboratory as part of a university or an existing research institute seems to be particularly appropriate, since this would allow its valuable equipment to be used for other purposes as well.

It goes without saying that, if required by actual conditions or requirements, the functions of the proposed laboratories can be extended to cover other functions or restricted to only a few of them.

## [illegible]

As a general rule, the functions of this laboratory are confined to the determination of the five main constituents of bauxite, using wet analysis techniques.

<u>Determination of the main constituents of bauxite</u>

Correct sampling is the first and most important condition for obtaining accurate and reliable analytical results. The sample must have the same properties of the bulk material, i.e. it must be a true average sample. Samples can be taken on site from the material prepared for transport (i.e. from the railway wagon or barge), from the railway wagon at the reception point or from the belt conveyor after crushing. Sampling conditions are usually laid down in national standards and delivery contracts.

Samples are required for both chemical analysis and the determination of the water content. In addition to containing chemically combined water, the bauxite coming directly from the mine has a relatively high "mine moisture content". After storage, the air-dried bauxite has a moisture content that is in equilibrium with the humidity of the atmosphere ("adherent moisture"). When chemical analyses are carried out on air-dried materials, the values obtained must be corrected to give values that relate to material oven-dried at 110°C.

Samples for chemical analysis are rough ground, their volume is reduced by quartering and the sample is ground further until it all passes through a 0.09-mm screen.

General methods for the chemical analysis of bauxites are to be found in handbooks of analytical chemistry [2,3,4] and elsewhere in the literature. Analytical procedures have been standardized internationally by the International Organisation for Standardisation (ISO) and nationally by bodies such as the American Society for Testing Materials (ASTM) in the United States, the Deutsche Industrie Normen (DIN) in the Federal Republic of Germany, GOST in the Union of Soviet Socialist Republics and the British Standards Institution (BSI) in the United Kingdom of Great Britain and Northern Ireland. However there is very little in the literature that deals with the specific details and techniques of bauxite analysis [illegible]. The larger alumina-producing companies have their own standard procedures for both analytical and technological tests.

Knowledge of the chemical composition of a bauxite is of supreme importance in estimating its technological and commercial value. In many cases, chemical analysis is confined to determining the five main constituents (loss on ignition, $Al_2O_3$, $SiO_2$, $Fe_2O_3$, $TiO_2$); if their total percentage is low, the quantity of other impurities is assumed to be constant [6].

Loss on ignition (LOI) is determined by heating the oven-dried sample at 1,100°C until a constant weight is reached, and from it conclusions can be drawn about the mineralogical composition of the bauxite, particularly if the individual mineral constituents can be separated by heating in stages, and if ignition tests are combined with the results of digestion tests performed under standard conditions.

Depending on the type of bauxite, various reagents are used to dissolve the ore for analytical purposes. Gibbsitic, gibbsitic-boehmitic bauxites are easily dissolved by treatment with mixed acid ($HCl + HNO_3 + H_2SO_4$). For diasporic bauxites, however, fusion with sodium carbonate and borax is necessary. The same technique is applied with boehmitic-diasporic bauxites and with red mud containing diaspore to obtain complete solution.

As a rule, $Al_2O_3$ is determined directly in the dissolved bauxite sample by volumetric analysis. Both the potassium fluoride procedure (titration of the released alkali at pH 10 with HCl) [2, p.51] and complexometric titration [7] are suitable. (The end point is determined by pH measurement.) For gibbsitic bauxites in particular, the $Al_2O_3$ content is often determined indirectly, using the formula $Al_2O_3\% = 100 - (SiO_2\% + Fe_2O_3\% + TiO_2\% + LOI + \Sigma\ impurities)$ [6]. In many cases, this procedure is no less accurate than the direct volumetric determination of $Al_2O_3$, and it permits a substantial increase in the laboratory's workload.

Great attention must be paid to the determination of the amount of silica in bauxites, since its percentage has a major influence on the economics of the Bayer process. Gravimetric analysis of silica (evaporation with HF) is a laborious but very accurate and reproducible procedure for determining the total silica content of bauxites.

From the technological point of view, it is not total silica but reactive silica (i.e. that which forms alumosilicates in the liquor) that is decisive. Since digestion conditions affect the value of reactive silica, these must be quoted together with the analytical results. Crystalline quartz can be distinguished from the silica contained in clay minerals (kaolinite) and from amorphous silica by analytical procedures, and the percentage of reactive silica is obtained by difference between total silica and non-reactive silica (quartz) [8].

Non-reactive quartz is present in significant quantities in some gibbsitic bauxites. This fact may have important economic advantages if the appropriate operating conditions are chosen.

$Fe_2O_3$ and $TiO_2$ are determined by volumetric analysis using bichromate [4, p.732] and by spectral photometry in the form of titanium acid peroxide, respectively. Reduction to $Ti^{3+}$ and titration with $FeCl_3$, using KSCN as indicator, [9] as well as precipitation with cupferron are also suitable for the determination of $TiO_2$.

Neutron activation analysis can be used successfully for the determination of $Al_2O_3$ and $SiO_2$ contents in bauxites [10]. An instrument developed in Hungary for this purpose (the Automatic Activation Analyser for Aluminium and Silicon, Type NTA-1527), can determine $Al_2O_3$ with an accuracy of ± 0.6 per cent and $SiO_2$ with an accuracy of ± 0.3 per cent. This procedure has a particularly bright future in the field of bauxite mining, because the portable equipment can be mounted on a truck and estimates of the bauxite grade can be made on site. However, this instrument cannot replace the wet analytical laboratory completely, since international specifications usually insist upon the determination of all five constituents.

Model laboratory type 1 can also be extended to perform analyses of aluminate liquor and red mud. For the latter, a flame photometer is needed for the determination of sodium content.

## Main units of model laboratory type 1

To carry out the functions of model laboratory type 1, the following rooms are required:

Store-room for bauxite samples
Bauxite preparation room (drying, size reduction, screening)
Wet analytical laboratory (solution of samples, chemical analysis)
Balance room
Spectral photometer room
Flame photometer room
Distillation and furnace room (water distillation, analytical drying ovens and furnaces)
Store-room for reagents, laboratory ware, auxiliaries, acids, etc.
Office
Lavatory

A specimen layout of model laboratory type 1 is shown in figure I. The floor space allocated to bauxite sample storage, bauxite preparation and the wet analytical laboratory is large enough to satisfy needs. if the laboratory is to be extended later to cover technological tests and research work. A room is provided for the flame photometer in order to carry out red mud analysis.

As a general feature, sliding doors are used throughout to save space as well as for reasons of traffic safety. The bauxite preparation room is well separated from the wet laboratory to prevent dust and noise from entering the laboratory. The spectrometer, flame photometer, balance and distillation rooms are all adjoining, preferably with glass partition walls between, and opening out onto a small corridor.

The bauxite storage room can be equipped with a window opening into the corridor through which samples can be handed in.

The layout shown in figure I is a compact arrangement, making the best use of the floor space (total floor area 153 $m^2$). It has the disadvantage, however, that if a later enlargement of the building becomes necessary, it is difficult to add other rooms easily. Later in this report, an alternative

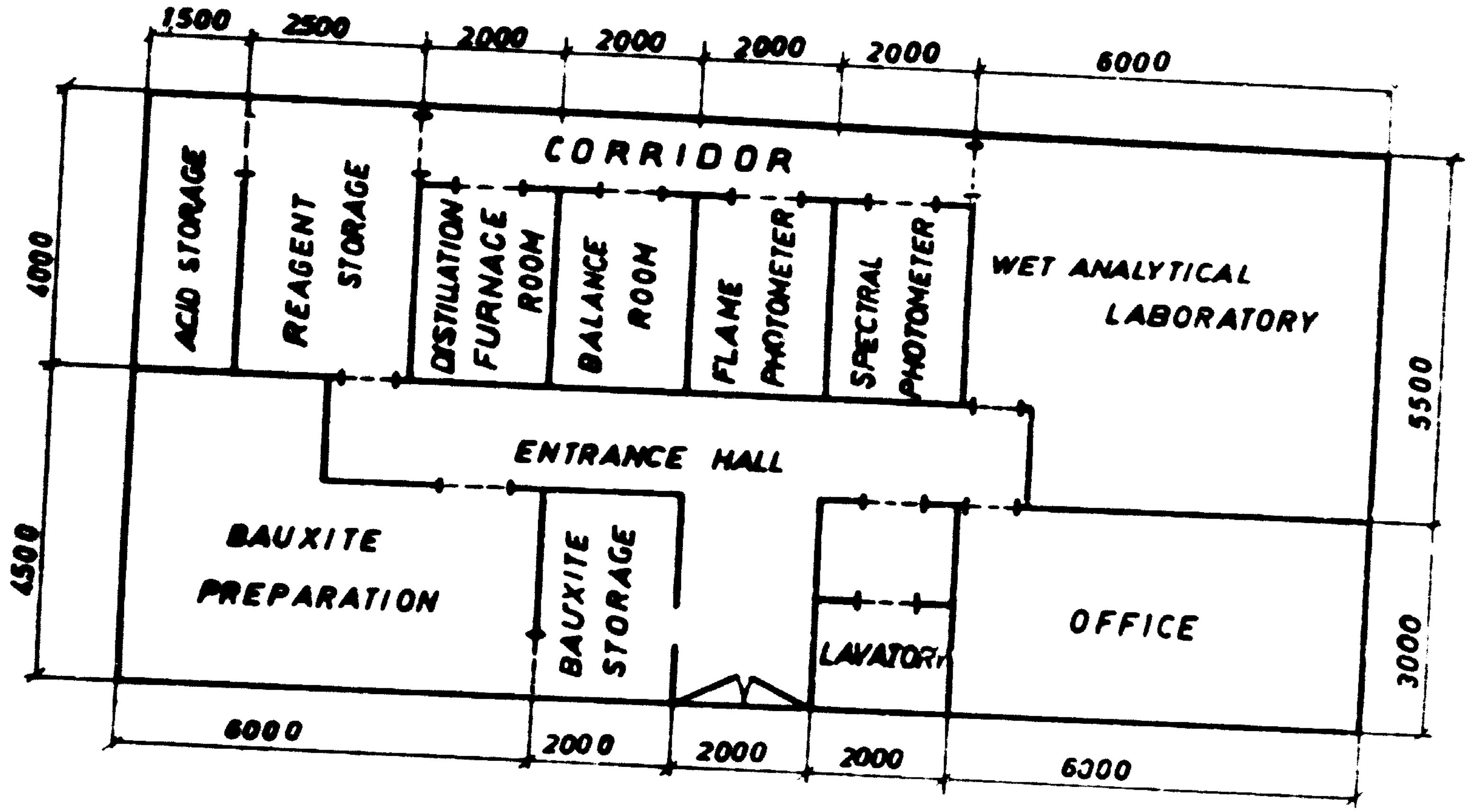


Figure I. Specimen layout for model laboratory type 1 layout of modular design that allows for enlargement of the building at a later date if required is presented (figure [illegible]). A detailed description of each room is given below.

Store-room for bauxite samples

The size of the sample required depends on the type of test to be performed. For chemical and phase analysis, 1-kg samples are adequate but, for process-evaluation tests, [illegible] -kg samples [illegible], depending on the testing programme.

The sample store is equipped with partitioned shelves. The shelf sections are numbered to facilitate the location of a sample at any time. Samples are grouped as follows:

> As received samples (before preparation). Large samples for technological testing are stored separately.
>
> Prepared (dried, ground, and homogenised) samples. These are passed to the laboratory for testing. Large samples in this group are also stored separately.
>
> Samples retained after analysis. A part of the sample is retained after analysis for periods that vary according to the type of tests. In the case of routine analyses, the sample is kept for one year. Representative samples and samples for technological tests are kept for five years, and some of them are kept permanently as reference samples.
>
> Red mud samples (and alumina samples, if these are tested in the laboratory). These are stored separately and retained for one year for control purposes. Representative samples are kept permanently as reference standards.

Bauxite preparation room

This room adjoins the bauxite store room. The sequence of operations is drying, crushing, screening and homogenisation. The room is therefore equipped with a large laboratory drying oven, a laboratory jaw crusher for rough size reduction, a ball mill and a vibratory mill for fine grinding, a mixing drum for homogenization, automatic screening equipment, a beam scale for weights up to 50 kg and a balance for weights up to 2 kg.

For analytical purposes, the sample is ground to a particle size of 0.09 mm. For technological tests, particles of 0.3- to 0.1-mm diameter are usually prepared; finer grinding is only needed for digestion tests on diasporic bauxite. Mechanical size reduction is essential; manual grinding and crushing cannot be used. Since size reduction and screening operations are inevitably accompanied by severe dust formation, the bauxite preparation room should be located as far away as possible from the wet laboratory and well separated from the rest of the building. This is also desirable in order to protect workers in other laboratories from the noise of crushers and mills.

Physical dressing tests, which may be required in due course owing to the properties and composition of the ore, can also be carried out in the bauxite preparation room.

### Wet analytical laboratory

This is a laboratory for chemical analysis with traditional equipment for the dissolution of samples and gravimetric and titrimetric analysis. It is provided with laboratory benches for a minimum of four workers, built-in cabinets, sinks and other auxiliary items. Two fume hoods are required for the treatment of samples. Fuel is supplied from propane-butane cylinders.

### Balance room

The balance room is equipped with at least two, but preferably three, analytical balances and one balance for weights up to 1 kg with a sensitivity of 0.01 g. It is important to have highly reliable balances so as to eliminate the need for frequent repairs.

### Spectral photometry room

This is a small room for spectral photometry and pH measurements. Samples for these tests are prepared in the wet analytical laboratory.

### Flame photometry room

The flame photometer required for determining the sodium content in red mud is located in a separate room. Minor analytical preparation operations are also carried out here.

### Distillation and furnace room

This room contains a distillation apparatus for supplying the laboratory with distilled water. The use of ion-exchanged water instead of distilled water is not recommended. Drying ovens and muffle furnaces for analytical purposes are also located here, since this room is not in constant use, and the heat from the furnaces thus causes the minimum of inconvenience. At least two ovens and two furnaces are needed to ensure continuity in case of breakdowns.

### Store-room for reagents and auxiliaries and acid store

This room is furnished with shelves, and reagents, auxiliaries, laboratory glassware, crucibles etc. are stored in sufficient quantities to ensure uninterrupted work. Acids are stored in a small adjoining room.

### Office

This is the office of the head of the laboratory. It is furnished with office furniture, built-in cabinets, files etc. The recording of test data, calculations, evaluation of test results, and administration (which should be kept to a minimum) are carried out in this office.

### Lavatory

The lavatory should be in part of the building that is easily accessible for all workers. In this study, changing-rooms and showers are not discussed, but it goes without saying that such facilities must be provided, preferably in a separate building. If this is impossible, they should be located at one end of the building.

## Requirements for model laboratory type 1

### Personnel

The personnel required for this type of laboratory is as follows:

1 chemist with university degree (head of laboratory)

2 operators (for bauxite sample preparation and sample storage)

1 chemist with technical school training (head of chemical analysis laboratory)

3 laboratory assistants (in chemical analysis laboratory)

1 unskilled labourer (cleaning, washing up etc.)

With this total complement of eight people, the laboratory can carry out 24 bauxite analyses per day (in respect of the five main constituents) or the equivalent in other types of analysis, such as that of red mud.

Equipment

The main items of equipment required for model laboratory type 1 are the following:

1 large laboratory drying oven with trays
1 laboratory jaw crusher
1 laboratory ball mill
1 vibration mill
1 beam scale for weights up to 50 kg with set of weights
2 balances for weights up to 2 kg ( sensitivity of 0.01 g) with set of weights
1 homogenising drum
1 automated screening apparatus with set of screens for screen analyses
2 fume hoods
24 platinum crucibles (25x30 mm)
10 platinum crucibles (40x50 mm)
10 platinum crucibles (50x55 mm)
4 magnetic stirrers
3 variable speed laboratory stirrers
2 infra-red lamps for drying
1 Mohr-Westphal balance
3 analytical balances with set of weights
1 pH meter
1 spectral photometer
1 conductometer
1 flame photometer
1 apparatus for water distillation
2 drying ovens for analytical purposes
2 furnaces for analytical purposes

## MODEL LABORATORY TYPE 2: A LABORATORY [illegible] AND TECHNOLOGICAL EVALUATION OF BAUXITE [illegible]

In addition to performing the functions of model laboratory type 1, this laboratory is equipped for:

- The determination of impurities in bauxite that are of significance from a process point of view
- Phase analysis of bauxites and red mud by means of standard digestion tests and thermal analysis
- The technological evaluation of bauxites
- Chemical analyses connected with the technological evaluation of bauxites (red mud, aluminate liquor)

### Functions of model laboratory type 2

### Determination of bauxite impurities of process significance

As far as the impurities that occur in bauxite are concerned, it is those that may cause $Na_2O$ losses, such as carbonates (calcite, dolomite), sulphates and sulphides that must most of all be determined. These impurities (as, for instance, the amount of CaO + MgO in diasporic bauxites) are often taken into account in fixing bauxite prices.

Organic matter and pyrite may cause operational difficulties in the Bayer process. For this reason, it is recommended that they be determined in certain types of bauxite. Industrial recovery of vanadium and gallium in the Bayer process may also necessitate the determination of these elements [5]. In bauxite, gallium is determined spectroscopically; in liquor, complexometric titration is recommended [11].

### Phase analysis of bauxites and red mud by standard digestion tests and thermal analysis

Knowledge of the mineralogical composition of bauxites is of primary importance, since it is the aluminium minerals that determine the type of bauxite (gibbsitic, boehmitic or diasporic) and even the procedure that must be used for dissolving the samples for chemical analysis [12]. Some examples are given in annex I to this report. Quantitative phase analysis of bauxites gives direct information about the alumina recovery that can be expected, as shown by the following examples.

Non-reactive silica (crystalline quartz) does not react with the digesting liquor and does not cause $Na_2O$ losses in the case of gibbsitic bauxites. As a result, ores with a high percentage of quartz give better results in processing than would be expected on the basis of their chemical composition alone. Aluminium incorporated in the lattice of iron minerals (goethite, hematite), which cannot be recovered with the Bayer process, can be detected by X-ray diffraction procedures. If no CaO is added to the digesting liquor, diaspore (which is present in quantities of 1 per cent and more in most bauxites) also remains undigested. Phase analysis of red mud makes it possible to determine the efficiency of digestion and the distribution of alumina losses among the individual mineral constituents.

In a laboratory that is not equipped to carry out complete quantitative phase analysis using physical chemistry procedures, it is still possible to make estimates of the individual aluminium minerals by using digestion tests under standard conditions at various temperatures. From these tests, alumina recovery can also be estimated, so that they can be considered to be a method for the technological evaluation of bauxite [13]. Digestion tests are usually carried out at 120°, 180°, and 230° to 240°C for 1 to 3 hours with solutions of 200 g $Na_2O_{caustic}$ per litre and using sample weights that do not permit the equilibrium molar ratio to be achieved.

At 120°C it is only the $Al_2O_3$ content of the gibbsite that is recovered. At 180°- to 240°C, the alumina content of boehmite is also recovered, whereas diasporic $Al_2O_3$ is recovered only in the presence of 3 to 4 per cent CaO, even at 240°C.

Thermal analysis gives direct information on the mineralogical composition of bauxites and red mud. These results, together with the results of standard digestion tests, may replace complete phase analysis by X-ray diffractometry in many cases. Thermal analysis is suitable for the quantitative determination of carbonates, sulphates and pyrite as well as aluminium and iron minerals [14, 15].

## Technological evaluation of bauxites

The practical value of a bauxite is decided by its suitability for the production of alumina. The tests discussed in this section are used to determine those properties of bauxites that influence their suitability for the Bayer process. Such tests are often restricted to the determination of digestibility. However, other important characteristics that have a significant effect on successful operation can also be determined under laboratory conditions.

The most important characteristics that should be tested are:

The grinding characteristics of the bauxite and the particle size required

The amount of digestible $Al_2O_3$ and the digestion conditions

The caustic soda losses to be expected

The amount of red mud formed and its separability (settling and filtration characteristics)

The effect of impurities (carbonate, sulphate, organic matter etc.) on operation and on the purity of the alumina produced

The prerequisite for chemical analysis and technological tests is a homogeneous sample. It is recommended that the grinding operation, which is essential to obtain such a sample, should be combined with grindability tests. Further tests are required to determine the particle size that ensures satisfactory digestion efficiency. Bauxites are usually ground to particle sizes of 0.1 to 0.3 mm. However, finer grinding is needed in the case of hard diasporic bauxites. Grinding tests are carried out in laboratory ball or rod mills. The size distribution is determined by screen analysis. For the finer fractions, sedimentation methods using a Sartorius balance or a sedimentometer are applied.

The simplest procedure for determining recoverable $Al_2O_3$ is to treat the bauxite samples under standard conditions with aluminate liquor. This test, however, does not yield any information about the operating conditions required, such as temperature [illegible] lar ratio. To provide such information, industrial conditions are simulated in laboratory batch tests, and the results of these tests are plotted to give digestion curves for various conditions. The temperatures and durations for these tests are selected on the basis of phase analysis results.

A series of tests using different sample weights are made for each set of conditions. Sample weights are so chosen that, with some of the samples, equilibrium molar ratio is reached in the liquor (i.e. the liquor becomes saturated with $Al_2O_3$), whereas with other samples the final molar ratio is higher than equilibrium and corresponds to the maximum practical recovery of $Al_2O_3$ from the bauxite. The digestion curves are then prepared from $Al_2O_3$ recovery plotted against the molar ratio [16, 17].

These digestion tests are carried out in steel autoclaves of [illegible], [illegible] and [illegible] ml capacity, depending on the requirements of future tests. The autoclaves are kept at constant temperature by being rotated in electrically heated oil, salt or air baths equipped with temperature control. The tests can be combined with preliminary or subsequent desilication. After digestion, the aluminate liquor is separated from the red mud by centrifuging, and the red mud is washed two or three times with distilled water, with intermediate centrifuging. Examples of digestion curves for gibbsitic, boehmitic and diasporic bauxites are given in annex II to the present report.

To simulate industrial digestion under laboratory conditions and to obtain larger quantities of red mud such as are needed for mud separation tests (by filtering and settling), vertical electrically heated laboratory autoclaves with volumes of [illegible] to 10 litres are used.

The economics of the Bayer process are strongly influenced by losses of caustic soda [17,18]. These losses can be estimated only partially from the analysis of red mud (which is carried out for preference by flame photometry) since they represent only combined and so-called "adsorbed" caustic; the effect of impurities such as carbonates, sulphates and organic matter in the consumption of caustic soda is not included. The washing in the preparation of red mud samples should not be excessive. The $Na_2O$ bonded in sodium alumosilicate is calculated according to a molar ratio of 1.33 moles $Na_2O$ to 2 moles reactive $SiO_2$. As far as losses due to titanium are concerned, the majority of the rutile and anatase passes unchanged into the red mud if the composition of the final liquor approximates to the molar ratio, i.e. if no free $Na_2O$ remains in the liquor. The losses arising from titanium minerals do not exceed 0.05 to 0.10 kg $Na_2O$ per kilogram of $TiO_2$ [17].

It is almost impossible to avoid extracting some phosphate, sulphate, vanadate, fluoride and organic matter. Other minerals such as pyrite and chamosite are attacked either slightly or not at all. Pyrite, however, severely impairs the settling characteristics of red mud. Special attention should be paid to the effect of calcite and dolomite. Their conversion to sodium salts depends upon the degree of dispersion of these minerals and on the temperature of digestion. In diasporic bauxites that require high temperatures, calcite and dolomite may be converted to sodium salts up to 80 to 100 per cent. For this reason, as mentioned earlier, the CaO content is often taken into account in the price of the bauxite. Losses of caustic resulting from the conversion of bauxite impurities into sodium salts can be calculated from the results of chemical and phase analysis of both bauxite and red mud and from the compositional changes in the liquor.

The anticipated quantity of red mud can be calculated from the composition of the bauxite and the red mud obtained in digestion tests. The separation characteristics are investigated by simulating industrial conditions in the laboratory. Settling characteristics are determined in sedimentation tubes. Calculation procedures exist [19,20] that permit industrial settling characteristics to be calculated from the data obtained in laboratory tests. By comparing the industrial and laboratory settling characteristics of known bauxites with the laboratory settling characteristics of the sample bauxite, conclusions may also be drawn about its probable behaviour under industrial conditions. Similarly, red mud filtration characteristics can be estimated by simulating industrial operations in the laboratory.

A procedure based on the transmission of the radiation emitted by the radioisotope thulium-170 has recently been developed at the Research Institute for Non-Ferrous Metals in Budapest. This makes a valuable contribution to the range of laboratory settling tests, since it permits the variation of solids concentration to be followed along the whole length of the sedimentation tube, even in the densest areas. The laboratory results compare well with the results of radioisotope tracer studies in alumina plants on digestion, settling and decomposition operations.

Finally, technological testing of bauxites should be extended to investigation of the effect of impurities in operations. Points of interest are the salt concentration in the process cycle, the amount of salt that must be eliminated, and the effect of detrimental constituents such as organic matter and pyrite.

The technological tests discussed in this section come within the potentialities of a well-equipped laboratory. In practice, the number and type of tests included in the programme of a laboratory will depend on the equipment available and on the demand.

## Analyses connected with the technological evaluation of bauxites (composition of red mud and aluminate liquor)

The chemical analysis of red mud does not differ significantly from that of bauxite, apart from the additional need for accurate determination of $Na_2O$, both as soluble and as combined $Na_2O$. For this purpose, flame photometry is the most reliable and accurate procedure [21]. If no flame photometer is available, the Na can be determined after fusion with boric acid [22]. As a rule, only caustic $Na_2O$, total $Na_2O$ and $Al_2O_3$ are determined in aluminate liquor [23]. In some cases, the percentages of $VO_3^-$, $PO_4^{3-}$, $SO_4^{2-}$, $CO_3^{2-}$, $F^-$, and $Cl^-$ (which accumulate in industrial liquors, as a result of recycling) are also determined, using normal analytical procedures, modified for this purpose [5].

## Main units of model laboratory type 2

Figure II shows a schematic layout for model laboratory type 2. Owing to the characteristic feature of this layout, that is, to the fact that all the rooms open into a central corridor, the building can easily be enlarged at a later date if required. By comparison with model laboratory type 1, shown in figure I, there are two additional rooms for the technological laboratory. The total floor area is 199.5 $m^2$. This layout can be enlarged to conform to the requirements of model laboratory type 3 by the addition of two rooms for the X-ray laboratory and one instrument room (indicated in figure II by broken lines) at one end of the building. This layout is advantageous if some future enlargement of the laboratory to form a complete research laboratory is anticipated. The total floor area of the enlarged building is 256.5 $m^2$.

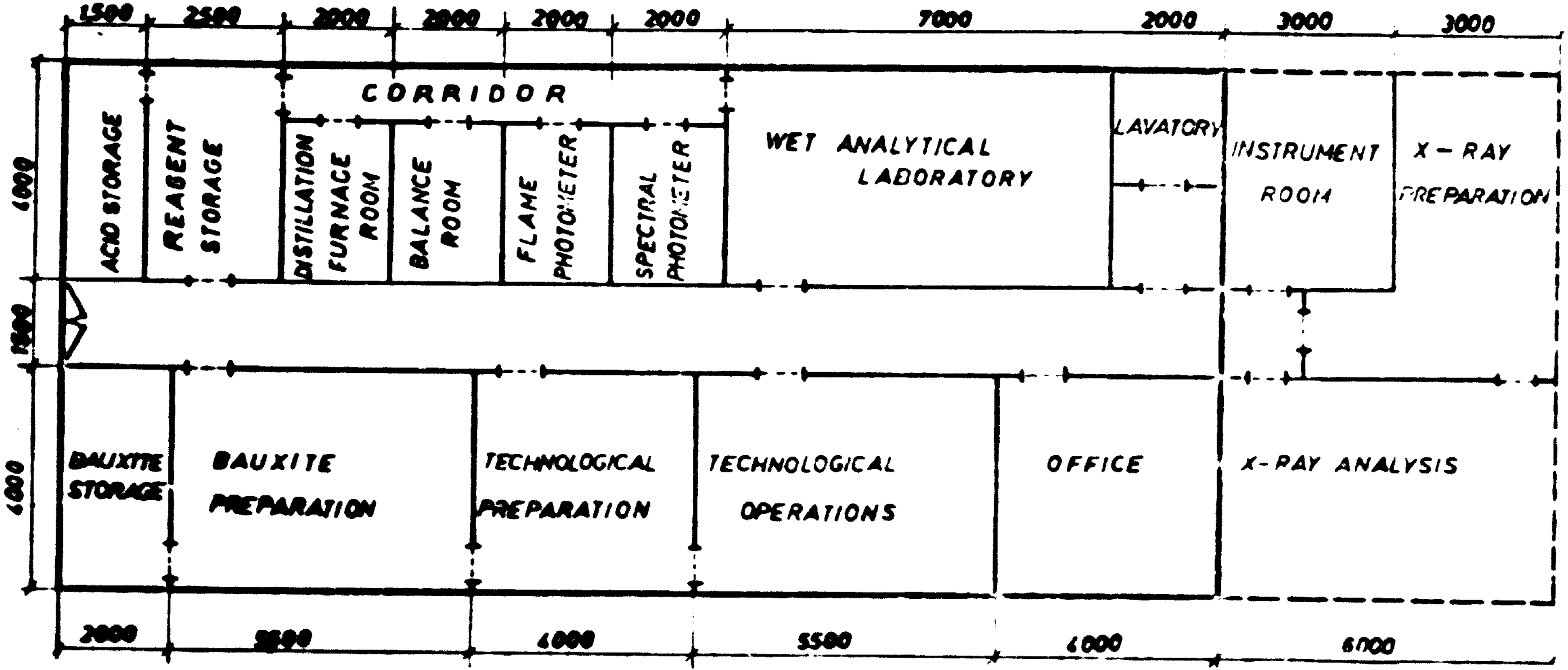


Figure 11. Specimen layout for model laboratory type 2

The analytical activities of model laboratory type 2 are carried in the same rooms as model laboratory type 1. The instrument for thermal analysis is located in the balance room.

The technological evaluation of bauxites takes place in the technological laboratory, which consists of two rooms:

A preparation room for technological tests (preparation of samples, preparatory chemical operations and liquor analyses)

A laboratory for technological operations (digestion, sedimentation, filtering and decomposition)

## Preparation room for technological tests

In this room, all the preparatory work for technological tests is carried out. Samples are weighed, aluminate liquors for digestion tests are prepared, red mud is washed and preparatory chemical work is carried out. Analysis of aluminate liquors before and after the digestion tests should also be done here. The equipment is similar to that for the wet laboratory for chemical analysis. Other necessary items are a balance for weights up to 1 kg (sensitivity 0.01 g), laboratory stirrers, vacuum filters and filter presses. The services required are electricity and gas outlets, running water and vacuum for filtering.

## Laboratory for technological operations

The operations of the Bayer process are simulated in this laboratory. The mills for the grindability tests, however, are not operated here but in the bauxite preparation room. The main items of equipment are: apparatus for laboratory digestion tests (set of 6 to 10 laboratory autoclaves in a thermostatically controlled and electrically heated oil or salt baths); laboratory centrifuges; apparatus for sedimentation tests (thermostatically controlled sedimentation tubes); thermostatically controlled atmospheric stirrer apparatus for four to six parallel tests (for investigating the atmospheric digestion of bauxite, preliminary desilication, causticisation, decomposition etc.); and furnaces for technological tests. The room is equipped with laboratory benches, cabinets, sinks, a hood above the oil bath, electrical and gas services and running water.

## [illegible]

**Personnel**

The personnel requirements are the same as those for model laboratory type 1 with the addition of:

- 1 chemist with technical school training (head of technological laboratory)
- 2 operators (for technological testing)
- 1 chemist with technical school training (for thermal analysis)

The total staffing of this laboratory is thus as follows:

- 1 chemist with university degree
- 3 chemists with technical school training
- 3 laboratory assistants
- 4 operators
- 1 unskilled labourer

With this staff of twelve people, the capacity for analysis of the laboratory is the same as for model laboratory type 1, i.e. 24 bauxite analyses in respect of the five main constituents or other equivalent analyses. In addition, phase analysis of two bauxite or red mud samples and tests to determine the characteristic digestion curves of one bauxite sample can be performed each day.

**Equipment**

The main items of equipment required for model laboratory [illegible], in addition to those required for model laboratory type 1, are the following:

- 1 balance for weights up to 1 kg (sensitivity 0.01 g) with set of weights
- 1 laboratory filter press
- 1 laboratory vacuum filter
- 2 variable-speed, heatable laboratory centrifuges for six tubes each
- 1 porcelain mill (1 liter) for grindability tests
- 1 porcelain mill (5 liters) for grindability tests
- 1 set of 10 autoclaves, 250 ml each, with thermostatically controlled oil bath (individual design and construction)
- 1 laboratory autoclave with stirrer, 10 litres
- 1 thermostatically controlled sedimentation apparatus with sedimentation tubes (individual design and construction)
- 1 thermostatically controlled atmospheric stirring apparatus for six parallel tests (individual design and construction)
- 1 polarisation microscope
- 1 air jet screen
- 1 sedimentometer
- 1 derivatograph

## MODEL LABORATORY TYPE 3: RESEARCH LABORATORY FOR BAUXITE TESTING AND ALUMINA TECHNOLOGY

Unlike model laboratories types 1 and 2, this type of laboratory is capable of the widest range of research and testing work in the field of analytical, technological and physical investigations connected with the alumina industry. Its functions include:

> Complete chemical analysis of bauxites and determination of trace elements. Among these analyses are those of soda and vanadium salts and deposits in alumina production.
>
> Complete phase analysis of bauxites and red mud by means of X-ray diffractometry, thermal analysis and infrared spectrometry.
>
> Determination of impurities in alumina and alumina hydrate products and testing of physical properties of alumina products.
>
> Investigation of sinter processes.

A still more advanced laboratory of this type, which differs most importantly from the one discussed here in that it incorporates a pilot plant, is described in detail in the second study in this series.[1]

### Functions of model laboratory type 3

### Complete chemical analysis of bauxites and red mud

Besides the classical wet procedures discussed in the previous sections of this report, X-ray vacuum spectroscopy is being used increasingly for the chemical analysis of bauxites. Within the last few years, considerable research has been carried out in this field, and the results have been in every way satisfactory. Recent work by Tertian [24,25] has led to the elimination of the inter-element (matrix) effect. As a result, the accuracy of determining the main constituents of bauxite by this procedure is now equal or superior to that of the wet methods. There is the important additional advantage that both measurements and the interpretation of the data can be fully automated, so that a very high performance is achieved. It is only the sampling and the preparation of the samples that is somewhat difficult.

---

[1] See "Analytical methods for testing bauxite, alumina and intermediate products" (UNIDO/ITD.171), Section F.

X-ray fluorescence analysis of bauxites is so highly developed that it is used in the automation of the Bayer process. It is successfully applied by Montecatini-Edison in Italy, at the Vereinigte Aluminium-Werke AG in Bonn, in th Geochemical Research Laboratory of the Hungarian Academy of Science, in the Research Institute for Non-Ferrous Metals in Budapest, at the alumina plant at Almásfüzitő (Hungary) and elsewhere. An adaptation of this method for use in the analysis of red mud is being developed [26]. However, the prospects are not so good as with bauxites, since the low atomic number of sodium does not permit $Na_2O$ to be determined.

Emission spectroscopy, spectrometry, polarography and neutron activation analysis are all suitable techniques for determining trace elements in bauxites and red mud. Analyses of the soda salt and vanadium salt that are precipitated in the Bayer process cycle and analyses of the deposits formed in the processing equipment are performed by both wet analytical and instrumental methods.

## Complex phase analysis of bauxites and red mud

Accurate determination of the mineralogical composition of bauxites and red mud is possible only by the application of modern procedures, particularly those of thermal analysis, X-ray diffraction and infra-red spectrometry. Crystal optical investigations are also valuable for identifying individual phases and for determining the texture of the bauxite. These procedures are fully established at the present time, not only in research work, but also in industrial practice. In the Almásfüzitő alumina plant, for example, the digestibility of the bauxite and the distribution of $Al_2O_3$ losses in the red mud are regularly controlled by X-ray diffraction [27].

Among the procedures mentioned, X-ray diffraction yields the most detailed information, since all of the mineral constituents of bauxite can be identified at detection limits of the order of 0.1 per cent, and the reproducibility and accuracy of the procedure (1 to 2 per cent) are excellent. The fact that the aluminium content of alumogoethite and alumohematite can also be determined is another advantage [17,28]. As a result of the work of Bárdossy, quantitative phase analysis of both bauxite and red mud have now been applied successfully for several years in the Geochemical Research Laboratory of the Hungarian Academy of Science, in the Research Institute for Non-Ferrous Metals in

Budapest and at the Almásfüzitő alumina plant. Details of the procedure are given in the literature [17,27,29].

Quantitative phase analysis of bauxites by thermal analysis methods [14,15] is particularly suitable for determining the water content combined in different forms and the percentages of carbonate, sulphate and pyrite. Infra-red spectrophotometry is successful for the qualitative and semi-quantitative determination of the aluminium minerals in bauxite and red mud and for the identification of individual clay minerals [30]. Electron micrographs can be used to determine crystal dimensions. Although electron probe microanalysis is informative about the distribution of trace elements and their correlation, electron microscopes and electron probe equipment are too expensive for the model laboratory recommended in this report.

Testing of alumina hydrate and alumina

If the laboratory is located at an alumina plant, it can assume the function of the control laboratory, with the addition of some extra equipment. The primary control task is to check the purity of alumina hydrate and alumina by chemical analysis. Usually, $SiO_2$, $Fe_2O_3$, $TiO_2$, $ZnO$, $P_2O_5$, $V_2O_5$ and $Na_2O$ are determined by spectrometry, polarography and spectral analysis [5]. Analytical procedures for these are laid down in standards and in delivery specifications. An as-yet-unpublished X-ray fluorescence method for the determination of $SiO_2$, $Fe_2O_3$, $TiO_2$, $CaO$, $ZnO$ and $V_2O_5$ in alumina has been developed in the Research Institute for Non-Ferrous Metals in Budapest. Its results are in full agreement with those from wet analysis.

Since specifications for alumina are becoming increasingly strict, it is essential that its physical properties should be tested regularly. Specific gravity, bulk density, percentage of $\alpha$-$Al_2O_3$, granulometric composition, angle of repose, rehydration and index of absorption are determined according to ISO Standard Recommendations. Only simple equipment is needed for these tests.

Investigation of sintering processes

Laboratory methods have been developed for simulating pyrogenic attack on low-grade bauxites and red mud. The material is sintered with $Na_2CO_3$ and $CaO$ on the tray of an electric furnace at a specified temperature for a given period of time, and the sintered product is extracted under standard conditions of liquor composition, temperature and duration. The object of investigations of this kind is to determine optimum sintering and extraction conditions for an unknown sample. Standard procedures have been established for various types of raw material.

Non-bauxitic raw materials are investigated in a similar way but under different conditions. In the USSR, for example, nepheline and alunite are regularly tested at the VAMI Research Institute in Leningrad, under standard conditions in the laboratory to determine the $Al_2O_3$ recovery that may be expected.

Physical procedures, such as hot-stage microscopes and heated X-ray chambers, are also used successfully for investigating sinter processes. Among other tests used are granulometric analysis and porosity tests of the sintered products. The mineralogical composition of the raw materials, sintered products and extraction residues is determined by the prodedures discussed above in the section on complex phase analysis, primarily by X-ray diffraction.

## Main units for model laboratory type 3

A very flexible layout that permits progressive enlargement of the installation from model laboratory type 1, through model laboratory type 2, to model laboratory type 3 is presented in figure III. The basic building for model laboratory type 1, which has an area of 162.5 $m^2$, is characterized by a front entrance and a central corridor that runs the length of the building; it is shown with solid lines in figure III. Extension can be done simply by the addition of rooms at the ends. Model laboratory type 2 can be obtained by adding two rooms shown by broken lines, at the left of the building for the technological laboratory, with a combined area of 38 $m^2$, for a total area of 200.5 $m^2$. The building can be further enlarged to permit the complete installation of model laboratory type 3 by enlarging it on the right end to house the X-ray laboratory and the instrument room, shown by broken lines, with a combined area of 57 $m^2$, for a total of 257.5 $m^2$. Side entrances can be put at the ends of the building, if desired, and the width of the central corridor can be made 2 m, rather than the 1.5 m shown in figure III.

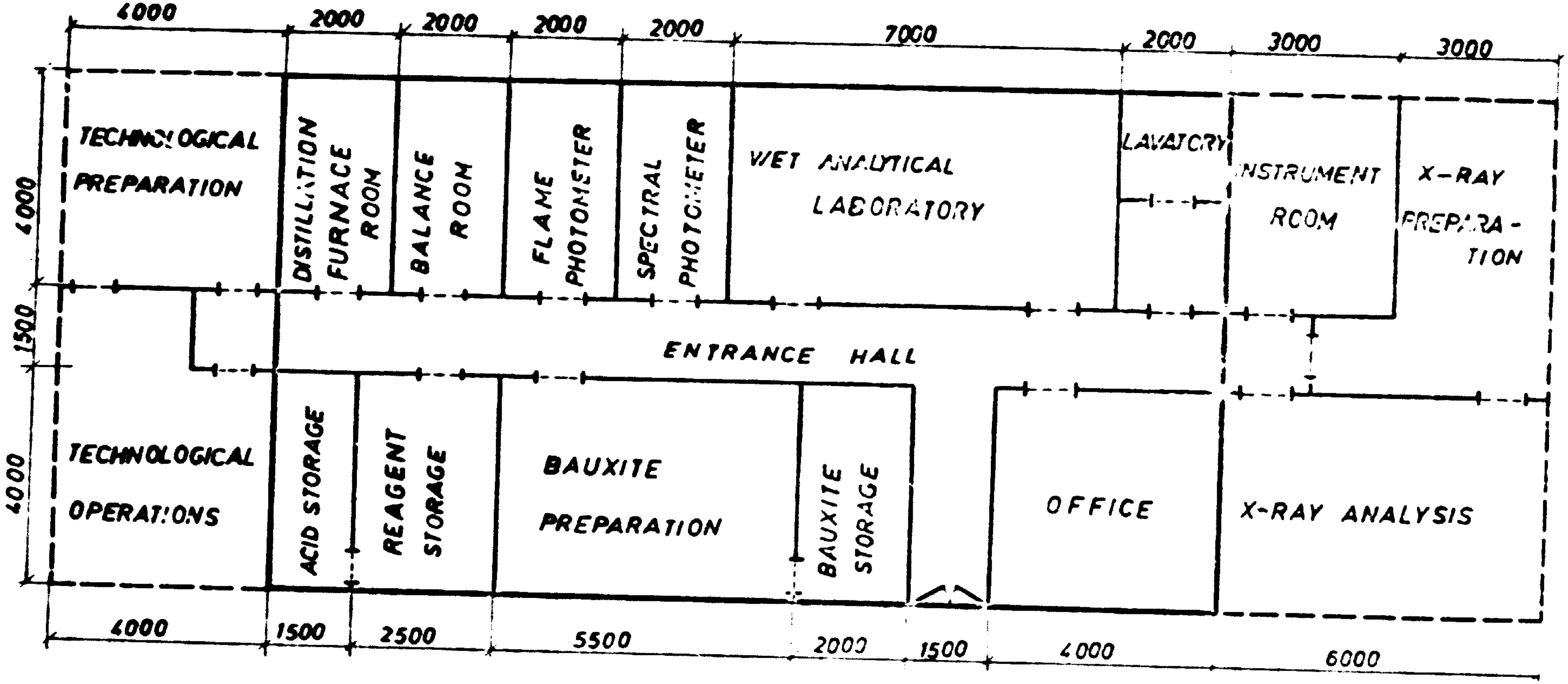


Figure III. Specimen layout for model laboratory type [illegible]

By comparison with model laboratory type 2, the functions of model laboratory type 3 demand an X-ray laboratory and a laboratory for instrument testing. Tests of alumina products and studies of sintering processes require some additional equipment, but no extra rooms are needed. Instruments for physical tests on alumina and equipment for preparing sinter mixes and for leaching the sintered products are placed in the preparation room of the technological laboratory; the furnaces are in the operations laboratory. However, if it is expected that a large number of tests will have to be performed, it is recommended that the floor areas of these rooms be increased.

## X-ray laboratory

For X-ray work, a separate laboratory consisting of two rooms is required; the larger one, with a minimum floor area of 20 $m^2$, is for the vacuum diffractometer and the vacuum spectrograph; the smaller one is for specimen preparation and data evaluation. A small mill for grinding the samples to fine powder and equipment for preparing the specimens by fusion techniques are also located in this room.

With the X-ray diffractometer it is possible to carry out quantitative phase analysis of bauxites, red mud, alumina hydrate, alumina and deposits in alumina plants, i.e. an almost unlimited determination of the mineralogical composition of a wide range of materials. X-ray vacuum spectroscopy, on the other hand, is a valuable method of quantitative chemical analysis (exception for elements with low atomic numbers) for determining the main constituents, impurities and trace elements, for example, in bauxites and red mud and the impurities in alumina product. However, the preparation of samples for this procedure is very laborious. If it is to be used for routine tests, one or two people will be needed for the preparation of samples.

## Instrument room

This laboratory is intended to complement and control the data obtained by phase analysis and technological tests. Microscopes are needed for crystal optical investigations of the phase composition of bauxite, of the $\alpha$-$Al_2O_3$ content in alumina etc. Microscopes with stages that can be heated are needed for investigating sintering processes. Instruments of both the camera type (Reichert) and the Leitz type are suitable (see list of equipment below).

A rapid and accurate method of determining granulometric compositions is often needed. In addition to screen analysis, a sedimentometer (operating on the photometry principle) or a sedimentation balance are recommended for analysing fractions below 60 μm.

The instrument room must have electricity services and running water. A small mill with a capacity of a few grams for fine grinding is needed for the preparation of samples for thermal analysis.

## Requirements for model laboratory type 3

### Personnel

In addition to the staffing listed for model laboratory type 2, the following are needed:

1 chemist with university degree (for instrumental analyses)

1 physicist with university degree (head of X-ray laboratory)

1 chemist with technical school training (preparation of specimens for X-ray analysis and X-ray measurements)

This means that the total staff for model laboratory type 3 should be:

2 chemists with university degrees

1 physicist with university degree

4 chemists with technical school training

3 laboratory assistants

4 operators

1 unskilled labourer

With this staff of fifteen people, model laboratory type 3 will be capable of performing all of the testing and research tasks connected with the alumina industry.

### Equipment

The main items of equipment required for model laboratory type 3, in addition to the equipment required for model laboratories types 1 and 2 are the following:

1 furnace for technological tests

1 granulometric analyser

1 sedimentation balance

1 heatable microscope

1 heatable microscope

1 BET apparatus for measuring specific surfaces
1 infra-red spectrophotometer
1 fine-grinding mill for X-ray specimens
1 X-ray diffractometer
1 X-ray vacuum spectrograph

## GENERAL COMMENTS ON SETTING UP MODEL LABORATORIES

### Organisation

The head of the laboratory should be an expert in all the testing methods used in the laboratory, i.e. in classical and instrumental analyses and technological tests, depending on the type of laboratory. Administrative work should be restricted to analysis certificates and records.

Material is drawn from the store-room with the approval of the head of the laboratory. One of the workers in the wet analytical laboratory is then made responsible for it.

All four of those working in the wet analytical laboratory should be experienced in all the operations performed there, including the use of analytical balances, spectral photometer and pH meter. One of the chemists with technical school training and one of the laboratory assistants should be trained in the use of the flame photometer. One of the mechanics should be trained to carry out minor repairs on the instruments.

### Training of personnel

The training of personnel can be done in two ways:

By giving special training to the senior workers in the laboratory (the chemists with university degrees and with technical school training) at a similar research institute or industrial laboratory. They can then, in their turn, train the laboratory assistants and operators.

By on-site activity by experts, in parallel with the organizational work of the laboratory. For this purpose, three experts with university degrees (one analytical chemist, one technologist and one X-ray physicist) are required for a stay of about six months. This period is adequate for training the personnel and starting up the laboratory.

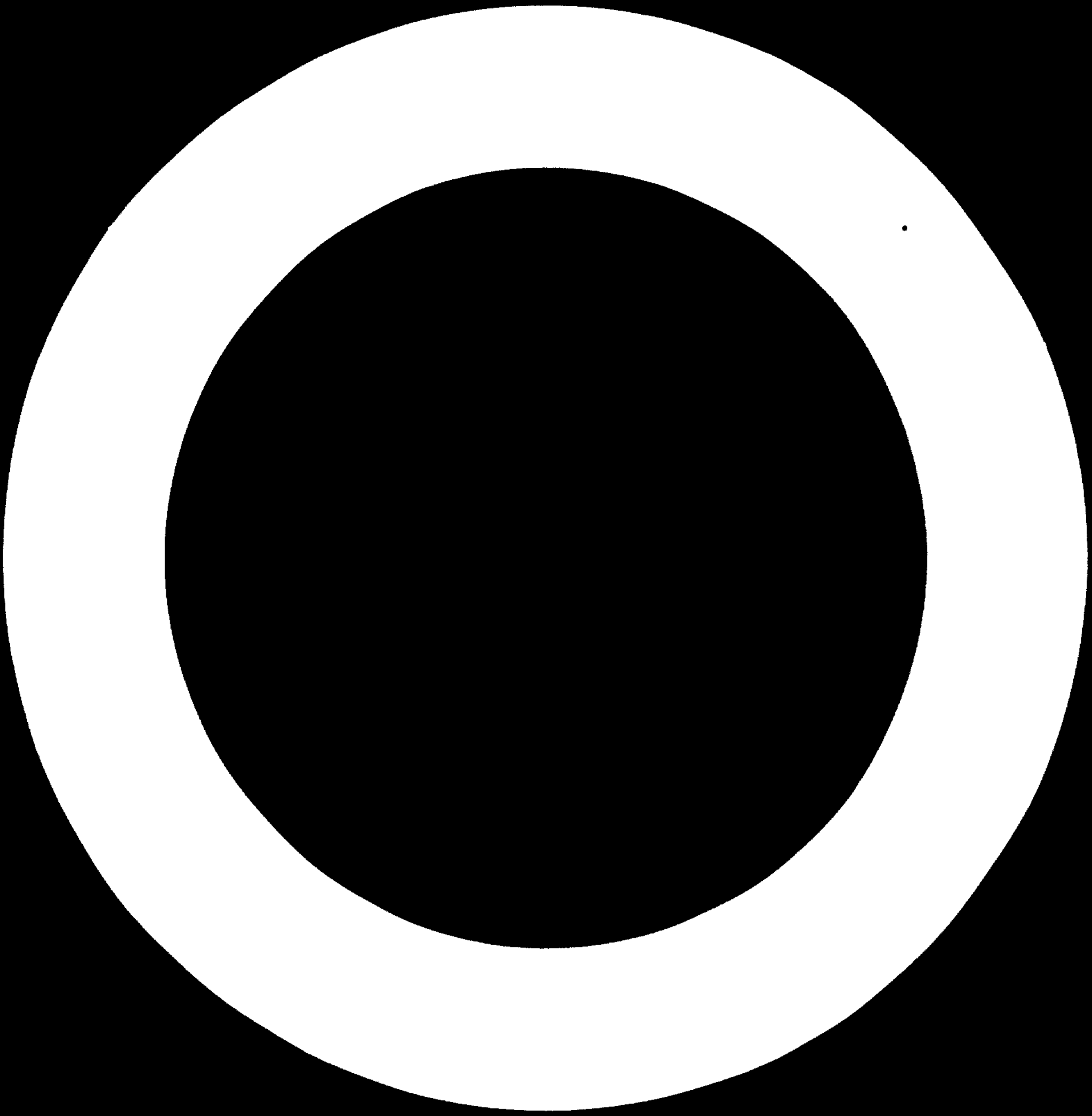
The latter alternative seems to be the more expedient. In this case, however, it is desirable that the head of the laboratory be sent on a study tour for several months in order to gain experience.

## Purchase of equipment

The complete equipment for model laboratories can be purchased from any large company that sells laboratory equipment, such as Prolabo in France or Fischer in the United States of America. Special instruments such as X-ray equipment, infra-red spectrometer, hot-stage microscopes etc. should be purchased direct from the manufacturers. Apparatus of an individual design that is not available commercially can be manufactured in the workshops of any large alumina company, such as the Research Institute of the Hungarian Aluminium Trust.

## Reference standards

Reference standards for the calibration and adjustment of instruments are needed for chemical and phase analysis and for technological testing. For this purpose, bauxite and red mud samples that have been exhaustively tested in every respect (i.e. chemical and mineralogical composition and technological behaviour) are used. Such samples are rather expensive, but they are essential when a laboratory is being set up. Reference standards cannot be purchased commercially but are available from the laboratories of aluminium companies.



## Annex

[illegible]

As an example of a complete phase analysis, the experimental results on a Hungarian bauxite and of the red mud obtained from it in a Hungarian alumina plant by digestion at 220° C are discussed below.

X-ray diffraction patterns obtained with a Müller Micro III generator and a Phillips goniometer, using $CuK_{\alpha}$ radiation, are presented in Figure IV. The positions of the goethite reflections (4.152 and 2.425 Å, respectively) correspond to a substitution of 20 per cent by AlOOH. Since the bauxite in question contains 10 per cent goethite, this is equivalent to 1.2 per cent of the total $Al_2O_3$ in the bauxite being incorporated in the lattice of goethite.

The presence of diaspore is demonstrated both in the bauxite and in the red mud. From the fact that the reflection of cancrinite at 3.24 Å is more intense than the line at 6.35 Å, it may be concluded that cancrinite is the predominant phase of the sodium alumosilicate in the red mud. The molar ratio of $Al_2O_3$ to $SiO_2$ in cancrinite is 1 : 2. Since the percentage of sodalite is low, the molar ratio of $SiO_2$ to $Al_2O_3$ bonded in the form of sodium alumosilicate is only 2 : 1.02 (for industrial liquors the molar ratio of $SiO_2$ to $Al_2O_3$ in sodalite is assumed to be 2:1.10). Incomplete digestion is indicated by the boehmite line at 6.117 Å on the diffraction pattern of the red mud. However, hydrolysis losses are low, as demonstrated by the scarcely detectable reflection of gibbsite at 4.844 Å. In both diffraction patterns the heights of the peaks used for quantitative determination are indicated.

Figure V shows the derivatograms of the bauxite and the red mud obtained with a MOM Derivatograph Type Paulik-Paulik-Erdey (weight of sample 1 g, heating rate 10°C/minute). On the bauxite derivatogram, there is no clear separation of goethite from gibbsite and of boehmite from kaolinite. The presence of these minerals is indicated by the distortion of the respective peaks, but a quantitative determination would

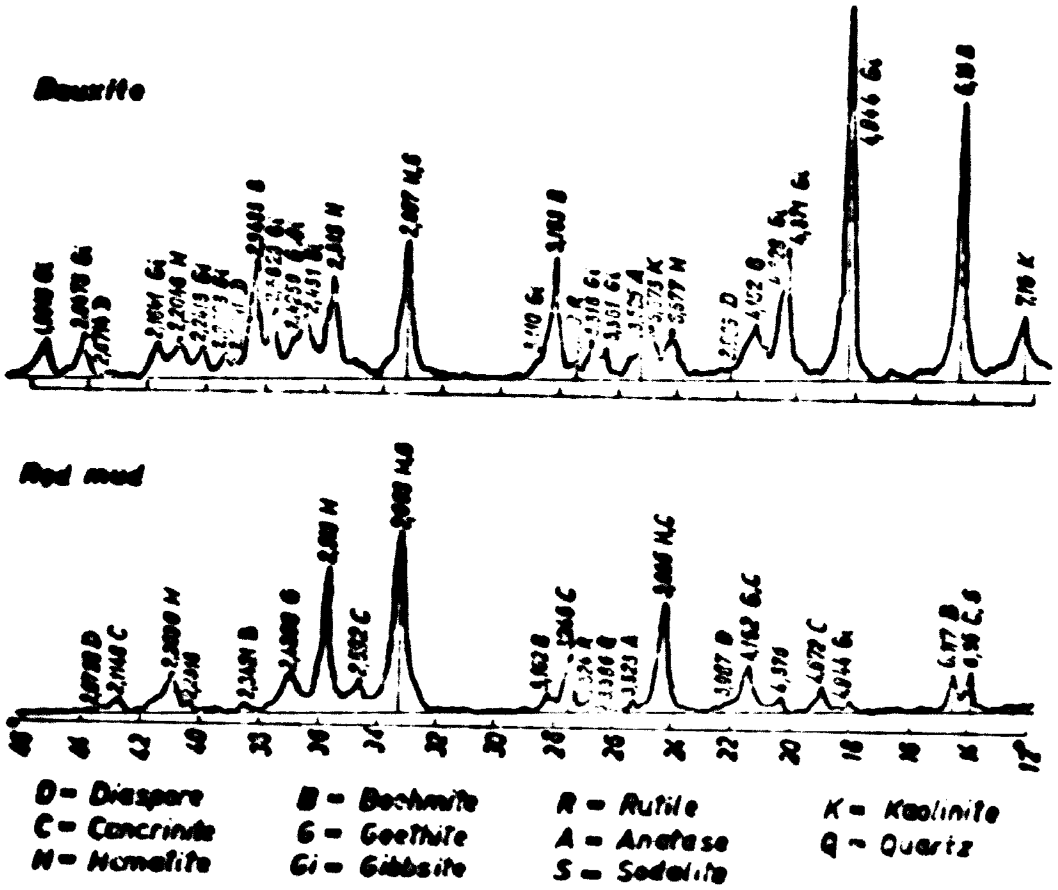


Figure IV. X-ray diffraction patterns obtained on Hungarian bauxite and red mud

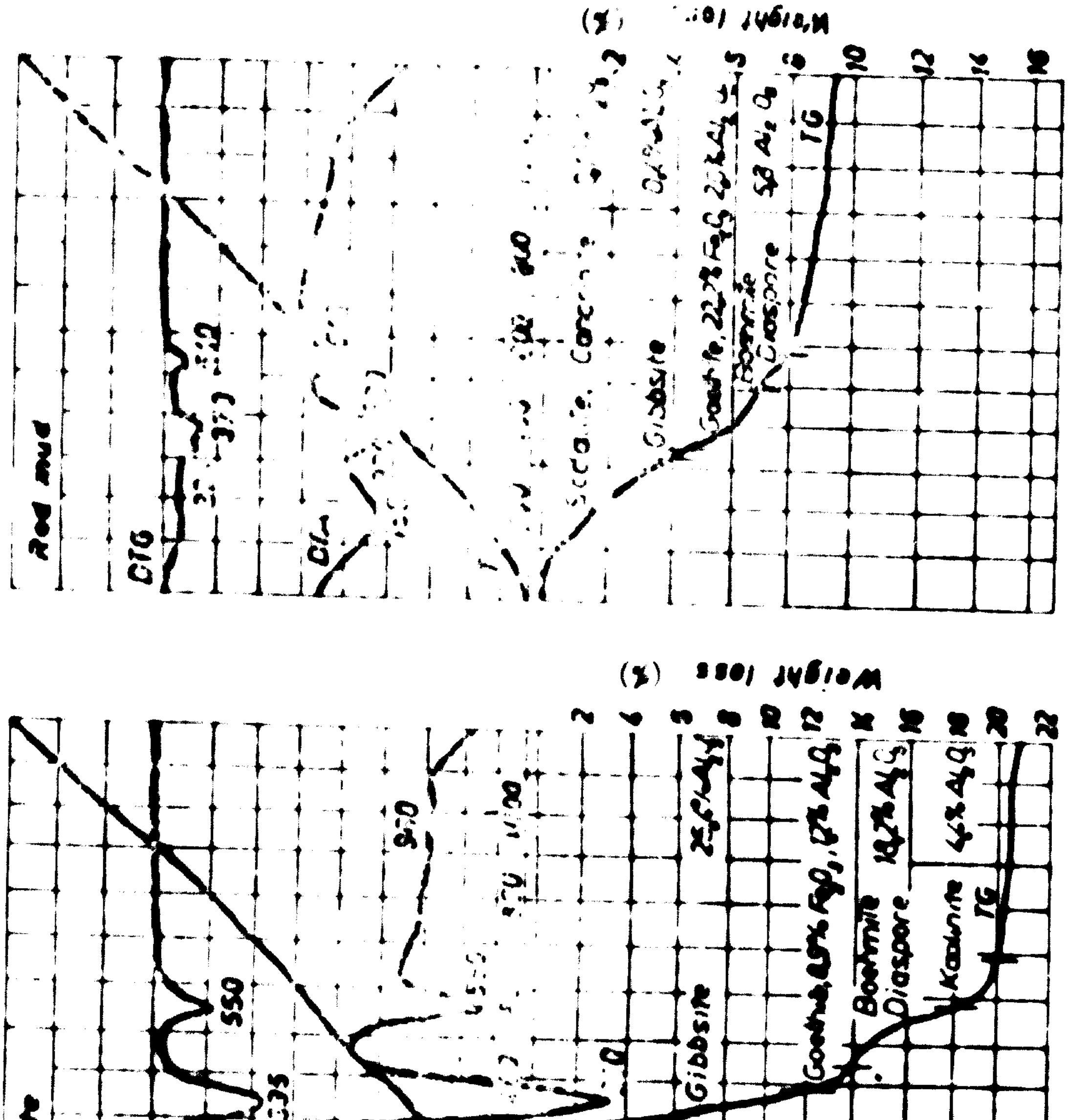


Figure 1. Derivatograms of Hungarian bauxite and red mud

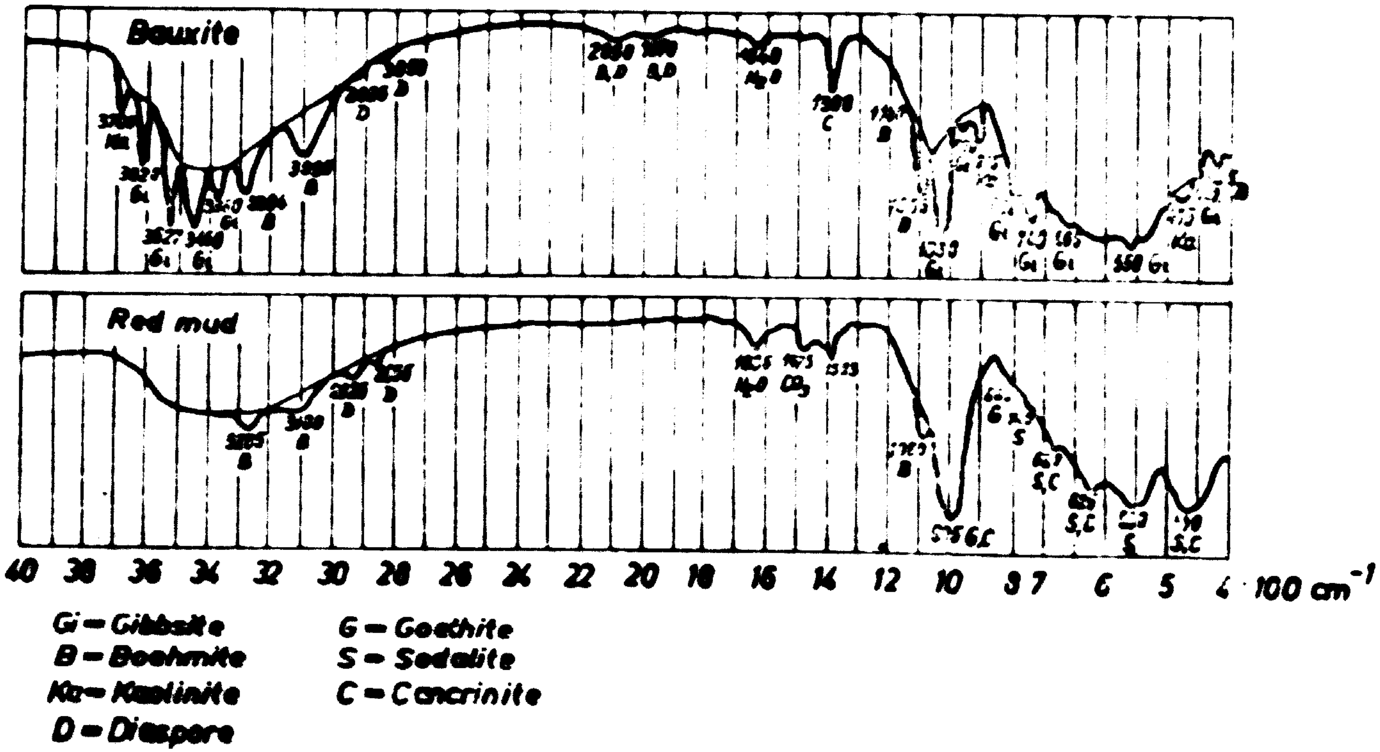


Figure VI. Infra-red spectra obtained on Hungarian bauxite and red mud be dubious. The peak obtained at 320°C on the derivatogram of red mud corresponds both to cancrinite and gibbsite (this is also confirmed by the X-ray diffraction pattern). The unusually high peak at 380°C, which corresponds to the endothermic water loss of goethite, seems to indicate a stabilising effect of the aluminium atoms incorporated in the lattice, since pure goethite loses water at 320°C. The endothermic reaction of both boehmite and diaspore is clearly demonstrated in the derivatogram. However, it is not possible to distinguish these mineral phases from each other.

The infra-red spectra of the bauxite and the red mud are presented in figure VI. Wave numbers and bands used for semi-quantitative determination are indicated. In the bauxite, diaspore cannot be discerned very clearly. In the red mud, however, its presence is so clearly manifested that a quantitative estimate can be made. The relatively high amount of undigested boehmite is also clearly shown. No gibbsite, however, can be detected. The table below summarises the results obtained by X-ray diffraction, derivatography and infra-red spectroscopy.

### Mineralogical composition of bauxite and red mud

| Constituent | Percentage |  |
|---|---|---|
|  | in bauxite | in red mud |
| Loss on ignition (LOI) | 20.8 | 8.1 |
| $Na_2O$ total | - | 8.5 |
| $Al_2O_3$ |  |  |
| in gibbsite | 25.4 | 0.4 |
| in boehmite | 17.3 | 4.0 |
| in diaspore | 0.9 | 1.8 |
| in kaolinite | 4.4 | - |
| in alumogoethite | 1.2 | 2.6 |
| in sodalite+cancrinite | - | 10.1 |
| Total $Al_2O_3$ | 49.2 | 18.9 |

| Constituent | Percentage | |
|---|---|---|
| | In bauxite | In red mud |
| $SiO_2$ | | |
| in kaolinite | 5.1 | - |
| in quartz | 0.5 | 0.9 |
| in sodalite+cancrinite | - | 11.8 |
| Total $SiO_2$ | 5.6 | 12.7 |
| $Fe_2O_3$ | | |
| in hematite | 12.4 | 26.9 |
| in goethite | 8.9 | 12.9 |
| Total $Fe_2O_3$ | 21.3 | 46.1 |
| $TiO_2$ | | |
| anatase | 1.7 | 3.3 |
| rutile | 0.6 | 1.3 |
| Total $TiO_2$ | 2.3 | 4.6 |

It can be seen from the data that, despite the high temperature of digestion, the quartz was practically non-reactive, and the $Al_2O_3$ in diaspore and alumogoethite was not recovered.

The expected recovery of $Al_2O_3$ (soluble $Al_2O_3$) can be estimated from the phase analysis data. Theoretical recovery is calculated using the formula:

$$\eta_{theor.}, \% = \frac{Al_2O_3\ total - 0.85\ SiO_2}{Al_2O_3\ total} \times 100$$

However, it is more correct to take only reactive silica into consideration.

For bauxites of the gibbsitic and boehmitic types (where no CaO is added to the digesting liquor), the following formula is recommended to estimate the recovery of $Al_2O_3$:

$$\eta_{\text{modified}},\ \% = \frac{Al_2O_{3(t)} - K_1 \cdot 0.85\ SiO_{2(r)} - K_2 \cdot Al_2O_{3(d)} - K_3 \cdot Al_2O_{3(g)} - Al_2O_{3(h)}}{Al_2O_3\ \text{total}} \times 100$$

where

the indices t, r, d, g, and h stand for total, reactive, diaspore, goethite, and hematite respectively, $K_1 \geqq 1$ is the number of $Al_2O_3$ moles per 2 moles of $SiO_2$ in sodium alumosilicate, $K_2 \leqq 1$ is the ratio of unextracted $Al_2O_3$ is diaspore, $K_3 \leqq 1$ is the ratio of unextracted $Al_2O_3$ incorporated in the goethite lattice.

In practice, the respective values are $K_1 = 1.00$ to $1.10$, $K_2 = 0.80$ to $1.00$ ($Al_2O_3$ is recovered from highly dispersed diaspore), $K_3 = 1.00$ and aluminium substitution in hematite is negligible (2 to 3 per cent). Thus, the modified formula for $Al_2O_3$ recovery can be written in a simplified form by assuming that $K_1 = K_2 = K_3 = 1.00$:

$$\eta^{*}_{\text{modified}},\ \% = \frac{Al_2O_{3\ \text{total}} - 0.85\ SiO_{2\ \text{reactive}} - Al_2O_{3\ \text{diaspore}} - Al_2O_{3\ \text{goethite}}}{Al_2O_3\ \text{total}} \times 100$$

To characterise the operation of an alumina plant, the introduction of the term "efficiency of digestion" $\eta'$ is recommended. This term includes losses attributable to undigested minerals and to hydrolysis and is obtained as the ratio of practical recovery $\eta_{\text{practical}}$ (which is obtained by calculation from the composition of the red mud) and modified theoretical recovery $\eta^{*}_{\text{modified}}$, such that:

$$\eta' = \frac{\eta_{\text{practical}}}{\eta^{*}_{\text{modified}}}$$

In the example, the various expressions for $Al_2O_3$ recovery have the following values:

$\eta_{\text{theor.}} = 91.3\ \%$ (quartz being non-reactive),

$\eta^{*}_{\text{mod.}} = 87.0\ \%$ ($K_1 = K_2 = K_3 = 1.00$)

$\eta_{\text{pract.}} = 82.4\ \%$

$$\eta' = \frac{82.4}{87.0} = 94.7\ \%$$

It is important to note that, in the case quoted, the modified theoretical recovery is lower than the theoretical recovery by 4.3 per cent owing to the undigested $Al_2O_3$ in diaspore and alumogoethite. On the other hand, the fact that silica is present in the form of non-reactive quartz has an upgrading effect on the quality of the bauxite, while impurities causing losses of caustic soda or giving rise to technological problems (for example, carbonates, sulphates, organic matter and pyrites) downgrade the ore. It is becoming more and more accepted for such characteristics as the carbonate content of diasporic bauxites to be included in commercial contracts as factors that may lead to price modifications.

The example discussed is intended to illustrate how a complete phase analysis of the bauxite and red mud contributes to a soundly based preliminary estimate of the $Al_2O_3$ recovery that can be expected under industrial conditions.

## Annex II

## CHARACTERISTIC DIGESTION CURVES OF THREE BAUXITES

The results of digestion tests and digestion curves for a gibbsitic, a boehmitic and a diasporic bauxite are presented by way of example.

The digestion curve of a gibbsitic bauxite containing 4 per cent silica in the form of quartz and another 4 per cent in the form of kaolinite is presented in figure VII. At a digestion temperature of 15[illegible] °C, quartz does not react with the digesting liquor. As a result, although the alumina contained in diaspore and alumogoethite is not recovered, a higher percentage of alumina is recovered than the value marked as "theoretical recovery" in figure VII, which corresponds to the recovery that would be obtained if the total $SiO_2$ content were reactive. The digestion curve shows the minimum molar ratio at which the total quantity of the extractable alumina is dissolved. The distribution of aluminium minerals in the red mud, which was calculated from the results of its phase analysis, is also presented in figure VII. It is obvious that the silica content dissolved in the liquor, i.e. the increase of silica in the liquor, must be taken into account to modify the composition of the red mud when recovery is calculated. It is important to note that digestion tests are not made with synthetic liquor but with "industrial" liquor, i.e. with liquor contaminated with salts as used in alumina plants. If uncontaminated liquor were used, higher losses of $Al_2O_3$ would arise, since in this case the anion X in the formula of sodium alumosilicate hydrate $3(Na_2O.\ Al_2O_3.\ 2SiO_2).\ Na_2X.aq$ which under industrial conditions stands for $CO_3^{2-}$, $SO_4^{2-}$, $2Cl^-$ and $2OH$ anions as well as for $2AlO_2^-$ anions, would represent $2AlO_2^-$ anions only.

Figure VIII shows the digestion curves of a Hungarian boehmitic-gibbsitic bauxite with a high percentage of goethite in the temperature range 180° to 300°C. The mineralogical composition of this bauxite is as shown below:

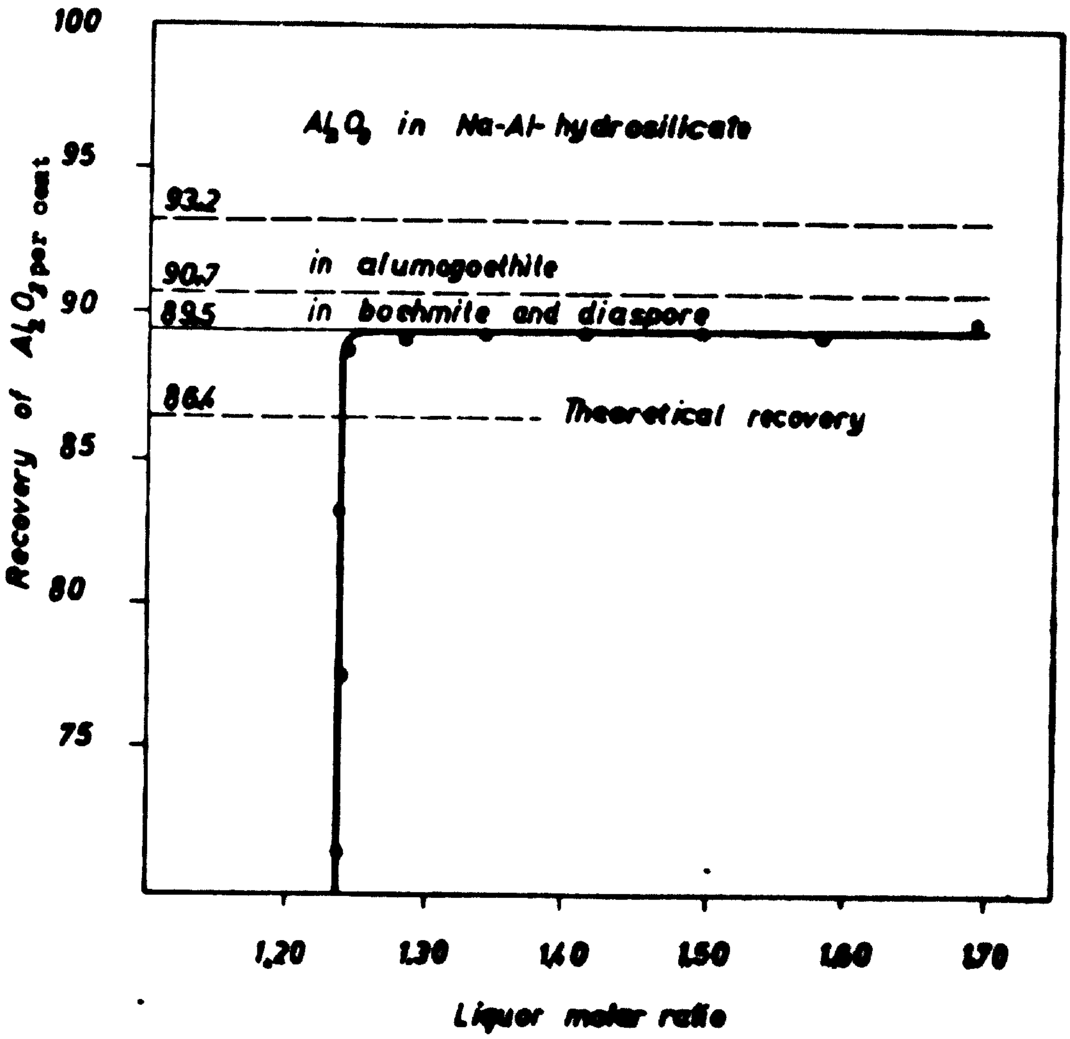


Figure VII. Digestion curve of gibbsitic bauxite

Digestion: 150°C, 0.5 hours
Digesting liquor: $Na_2O$ 179,8 g/litre $Al_2O_3$ 71,8 g/litre

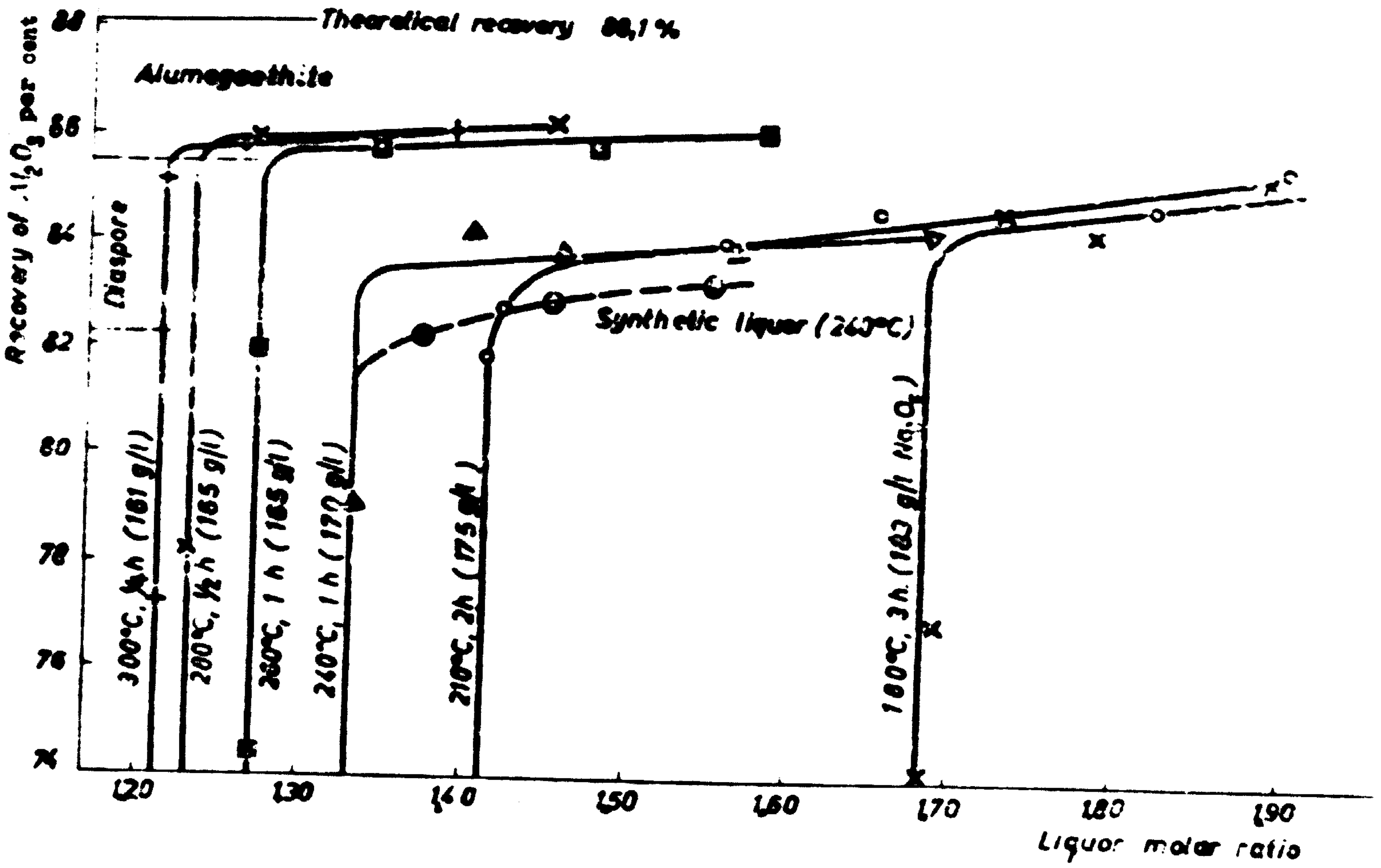


**Figure VIII.** Digestion curves of Hungarian boehmitic-gibbsitic bauxite

Digesting liquor: $Na_2O$ 233,0 g/litre $Na_2O_c$ 203,1 g/litre $Al_2O_3$ [illegible] g/litre
$SiO_2$ 0,65 g/litre

| Constituent | Percentage | Constituent | Percentage |
|---|---|---|---|
| $Al_2O_3$ | | $Fe_2O_3$ | |
| in gibbsite | 20.5 | in hematite | 6.1 |
| in boehmite | 22.2 | in goethite | 12.6 |
| in diaspore | 1.6 | Total | 18.7 |
| in kaolinite | 4.4 | | |
| in alumogoethite | 1.3 | | |
| Total | 50.0 | | |
| $TiO_2$ | | $SiO_2$ | |
| Anatase | 2.3 | in kaolinite | 5.4 |
| Rutile | 0.6 | in quartz | 1.6 |
| Total | 2.9 | Total | 7.0 |
| Loss on ignition | 19.4 | CaO | 0.6 |
| | | MgO | 0.32 |

Aluminium substitution in goethite, mole per cent ?

For this bauxite, the theoretical recovery of $Al_2O_3$ is 88.1 per cent. If aluminium combined in goethite is considered as unextractable, the modified recovery is 85.5 per cent. As shown in figure VIII, up to temperatures of 240°C the predominant part of diaspore remains unattacked, so that the modified recovery is only 82.3 per cent. In the calculation of the modified recovery, total $SiO_2$ was assumed to be reactive. Figure VIII, however, shows that a substantial part of the quartz does not react at 180° and 210°C.

The broken line in figure IX represents the digestion curve obtained with synthetic (salt-free) liquor. In this case, the higher alumina content of sodium alumosilicate results in a lower recovery of $Al_2O_3$ than with industrial digesting liquor.

The digestion curve of a boehmitic-diasporic bauxite at 240°C, without and with CaO, is presented in figure IX. The mineralogical composition of this bauxite is:

| Constituent | Percentage | Constituent | Percentage |
|---|---|---|---|
| $Al_2O_3$ | | $Fe_2O_3$ | |
| in boehmite | 39.2 | in hematite | 22.7 |
| in diaspore | 12.5 | in goethite | 3.6 |
| in kaolinite | 2.4 | in pyrite | 0.1 |
| Total | 54.1 | Total | 26.4 |
| $SiO_2$ | | | |
| in kaolinite | 2.3 | Loss on ignition | 11.9 |
| in quartz | 0.7 | CaO | 0.3 |
| Total | 3.0 | | |

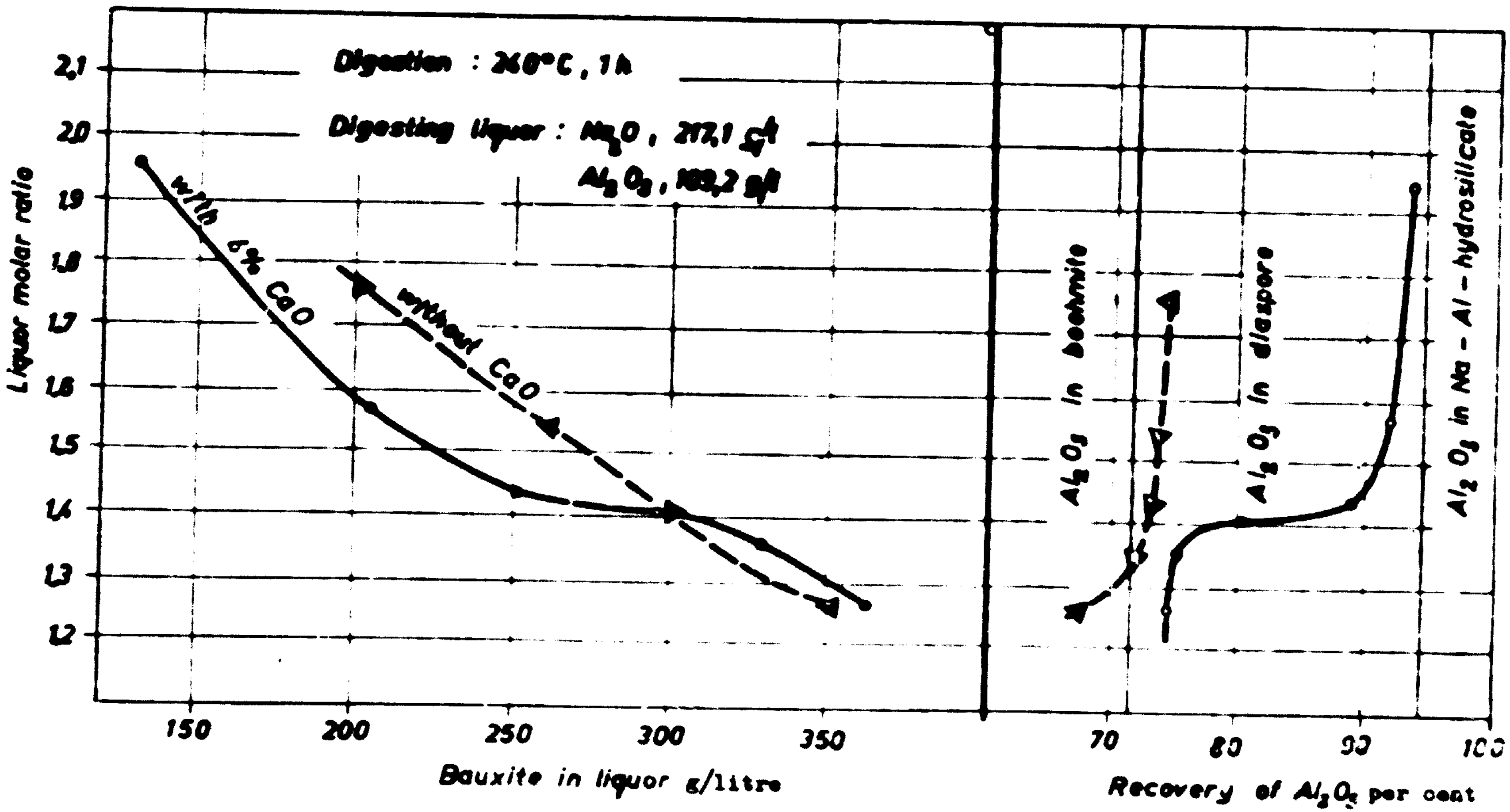


Figure IX. Digestion curve of a boehmitic-diasporic bauxite

Figure [illegible] shows that, even at [illegible] and with a relatively high molar ratio in the liquor, diaspore is not attacked if no CaO is added. Since boehmite is the first to be extracted, only liquor with a low molar ratio is left for diaspore in which it is insoluble. The distribution of aluminium among the mineral phases of the red mud has been determined by phase analysis. The digestion curves give information not only on the recovery of alumina but also on the optimum conditions for digestion.

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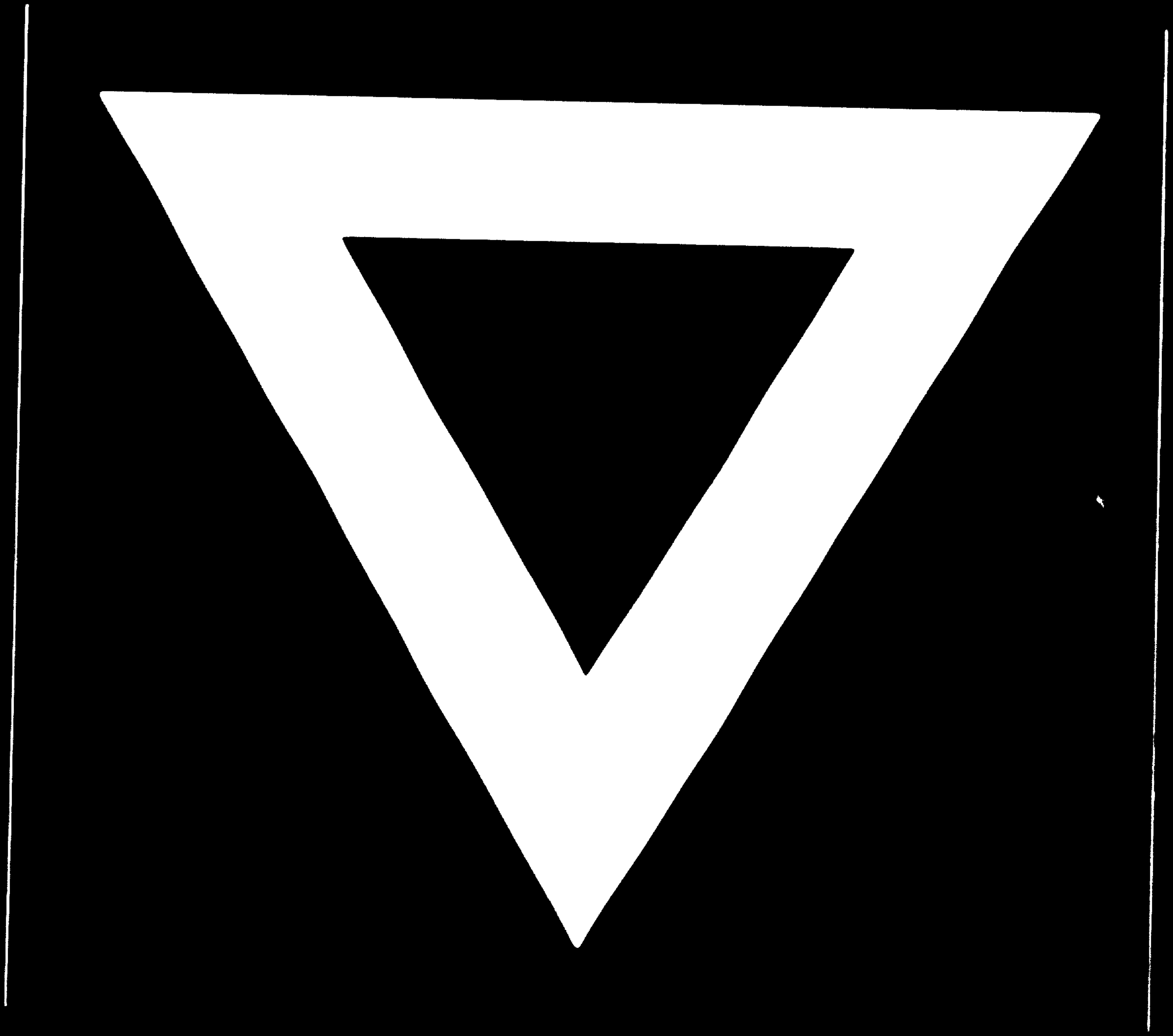

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