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United Nations Industrial Development Organization

GROUP TRAINING IN PRODUCTION OF ALUMINA

VOLUME 3

CHEMICAL ANALYSIS OF BAUXITE, RED MUD, ALUMINATE LIQUORS AND ALUMINA

ALUTERV-FKI
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VOLUME 3

CHEMICAL ANALYSIS OF BAUXITE, RED MUD, ALUMINATE LIQUORS AND ALUMINA

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1. INTRODUCTION

It is the Bayer-technology that is used worldwide in the industrial processing of the bauxites. This technology involves great demands on investigation and analyses. The composition of bauxite to be processed, the efficiency of desilication and digestion, moreover the getting into solution of the contaminants should be known. The efficiency of settling, filtration and precipitation has to be checked mainly by analytical methods. Plant control and process control is mainly based on analytical measurements, too and that is why plant operation without analytics in unimaginable. For that very reason it is necessary to deal in detail with the analytical problems of the alumina production.

When analysing bauxites one has to proceed on the basis of 4 aspects.

a) Surveying and determination of bauxite resources

b) Qualification during exploitation

c) Controlling the process of alumina production, preparation of balances

d) Accounts between supplier and consumer

When qualificating aluminas primarily the testing of those components is necessary which are undesirable for metallurgical processing.

Testing of red muds provides important information among others about the rate of alumina and caustic soda losses.

The analysis of aluminate liquors renders help for the control of the precipitation process and the reduction of contaminants in the precipitated alumina hydrate.

The many-sided investigation in the alumina industry and researching requires the whole verticality of the analytical procedures, including the conventional chemical and most up-to-date physical-chemical procedures

These are as follows:
Gravimetry
Titrimetry, potentiometry
Photometry, spectrophotometry
Thermometry
Optical emission spectral analysis
Atomic absorption analysis
Nuclear analytical methods
Spectrometric and X-ray spectrometric analysis

Particular agreement usually brought about between supplier and purchaser stipulates the standard specifications and testing methods to be applied for the determination of the individual components.

A separate problem is caused by the analysis of samples arising with different and varying compositions during the technological research work.

2. GENERAL ASPECTS OF THE METHODS USED IN BAUXITE, RED MUD, AND ALUMINA ANALYSIS. GRAVIMETRIC, TITRIMETRIC AND INSTRUMENTAL METHODS

Principle of the gravimetric analytical method:
A weighed portion of a sample of known quality is taken and the component to be determined is transferred mostly from the liquid phase into a form suitable for separation and identification. The component is weighed either in the elementary state or after being transformed into a coumpound of known composition. The determined component is expressed in terms of percentage of the charged quantity the calculation of which is carried out on the basis of the data obtained and according to the law of stoichiometry.

This investigation method is rarely adapted now in the alumina industry, however, it is still indispensable in some areas. For instance in the case of arbitration analyses and checking of results of instrumental measurements of the silica, sulfur content of bauxites and moisture and L.O.I. (Loss On Ignition) values the gravimetric method is used in every case. Similar practice is adapted at the testing of particular red muds or bauxites selectively separated.

At the volumetric (titrimetric) analytical method standard solution of a known concentration is added to the solution of the weighed test material the former being capable of entering into quick and full reaction with the component to be determined. The amount of component sought for can be calculated from the volume of the standard solution consumed. For the indication of the end point of reactions, were it not be perceived by the change of the colour of the solution itself, indicators are generally used which by changing their colour fairly indicate the termination of the reaction. Potentiometric and conductivity measurements may also be adapted. The volumetric testing procedures can be further broken into acidi-

-alkalimetry, oxidimetry, redoximetry, etc.

The titrimetric method is used for the determination of particular components of bauxites and red muds. The complexometric method is used for the determination of Al_2O_3 of the samples, or CaO and MgO-content exceeding 4 % in the samples.

The oxidimetric method is used for the determination of Fe_2O_3 and FeO the titrant being potassium dichromate. If the sample contains more TiO_2 than 5 % the determination is made by $FeCl_3$ standard solution.
Molar ratio and total caustic from the aluminate liquors is also determined by titrimetry.
Well proved method for the determination of chromium and vanadium content of samples is the potentiometric end point indicating procedure.

The photometric or spectrophotometric testing procedures find wide range application particularly for the determination of minor tracing components.
The photometric, or more exactly spectrophotometric measurements are based on the selective light absorption or more generally on the selective absorption of the electromagnetic radiation. The quantitative analysis is rendered possible on the basis of the Lambert-Beer's Law.
The light source and the cell containing the material to be tested, the light resolution unit, the photometer itself, the evaluating unit, a micro-ammeter or recording unit represent the basic elements of the photometers and spectrophotometers.
The light resolution unit is generally combined of colour filters at the photometers, while in the spectrophotometers monochromators are used.
There are spectrophotometers available for the application in the ultra-violet, visible and infrared ranges. Good resolving power is characterising the UNICAM and PERKIN-ELMER spectrophotometers. The spectrophotometric method is used for the

determination of TiO_2, V_2O_5, MnO_2, Ga_2O_3 and P_2O_5-content of bauxites and red muds. From the alumina the contaminants of SiO_2, Fe_2O_3, TiO_2, V_2O_5 and Cr_2O_3 are determined. From the aluminate liquors V_2O_5, Fe_2O_3, Ga_2O_3, etc. are regularly analysed.

The basis of the thermometric analytical method is the fact that every chemical reaction is accompanied by the change of heat content and consequently change in the temperature. This change of the temperature is measured with various sensors.

The thermometric analysis is applicable for cases where great change of enthalpy occurs and the reaction takes place quickly and quantitatively.

An instrument has been developed for this purpose in Hungary and it is well applicable for the analysis of aluminate liquors (total Na_2O . caustic Na_2O, Al_2O_3, CO_2), for the determination of the siderite content of bauxite and for carrying out of special physical measurements (i.e. adsorption heat, dilution heat). There is a possibility to extend the investigation over the determination of individual components of bauxite and red mud and the composition of vanadium salt.

Principle of emission spectral-analytical method:
The suitably dressed test material is excited. On the effect of excitation a light radiation takes place in the course of returning of the electron from the unstable higher energy level to the stable, lower energy level. The radiation beam is resolved by a prism or diffraction grating. The intensity of the resulting spectral lines is measured and the concentration of components in question is determined by evaluating curves plotted by means of the standards.

For the spectral analytical tests a quartz and a glass prism spectrograph and a spectrometer with ARL 35000 ICP excited monochromator are at our disposal.

The bauxite samples are tested partly in the dissolved state partly in the pulverized form:

- from the liquid sample aluminium iron, titanium and silicon content is measured by coupling inductively high-frequency a plasm excitation source.
  The temperature of the produced argon-plasm comes to about 9000 ^{o}K which - according to literary data - considerably reduces the adverse matrix effect disturbing the testing of the given element, or the interactions between the elements, or in some cases even eliminates it completely,
- from a pulverized sample the tracing contaminants such as beryllium, gallium, zinc, chromium, vanadium and manganese are tested by the Q-24 spectrograph.

Red mud is tested similarly to the bauxite: here the gallium content is determined.

The silicon, iron, titanium, vanadium content of the alumina is tested with the Q-24 spectrograph in a pulverized form.

From the aluminate liquor gallium is determined by means of the Scheibe-Ryvas method using excitation in an alternative--current interrupted arc.

When applying the atomic absorption method the material to be tested is brought to atomic state into the way of constant intensity light beams and the slackening of the intensity of the light is measured. Hollow cathode lamps are used as sources of light. The change taking place in the high-temperature area is indicated by a photometer equipped with a monochromator. For this purpose Pye UNICAM and PERKIN ELMER instruments are available. Main components of bauxite and red muds i.e. Fe_2O_3,

Al_2O_3, TiO_2, CaO, MgO and ZnO are determined with the atomic absorption method without aiming at the arbitration analysis accuracy. Emission flame photometry is used for the determination of Na_2O-content of the red muds. AAS is used for the determination of ZnO, MgO and CaO from the aluminate liquors. Flame photometry is used for the determination of Na_2O from the alumina and AAS for the determination of CaO, MgO, ZnO and CuO from the same.

The advantage of the method is its quickness and that it provides the possibility of the individual components to be determined without any separation as compared to those mentioned above.

The X-ray fluorescent analytical method has been developed in the last 20 years and has become extensively used. The elements present in the material to be tested should be excited in a way that each element emits its radiation of characteristic wave-length. Measuring the wave-length of the emitted X-ray the qualitative identification of the elements being present can be carried out. If the intensity of radiations of various wave-lengths is also measured the amount of the individual elements can be determined, too. The method can be used for the determination of any main and contaminating components ranging from 9F to 92U.

Recently there is a possibility to carry out quantitative determination of SiO_2, Al_2O_3, Fe_2O_3, TiO_2 and CaO from the bauxite and the red mud by using the "solid solution" (bead--casting) dressing method

In the course of sample dressing the amount of L.O.I. can also be determined.

From the alumina the SiO_2, Fe_2O_3, V_2O_5, CaO and ZnO-content is determined by means of this method.

Nuclear analytical measurements find rather wide range of application in the industry. Their main goal is the quick data supply. When using the neutron-activation process particles are produced which are charged by an ion-source of a neutron generator and after that they are accelerated and focussed in vacuum by means of ion optics while they reach the targets suitable for producing neutrons being able to release.

Deuterium and tritium are used most frequently which are bombarded by neutrons.

The advantage of the neutron generators lies in their comparatively easy location, and in their low demand on radiation protection because radiation danger occurs only during operation.

The Geophysical Institute has recently developed an instrument which is equipped with an Am-Be neutron source. The unit can be used for the determination of Na_2O, SiO_2 and Al_2O_3 in the bauxites and red muds on the basis of the principle of neutron activation and for the determination of CaO, TiO_2 and Fe_2O_3 by using the radioisotopic excitation X-ray emission analysis.
The neutron activation analyzer is being used for several years for the determination of SiO_2 and Al_2O_3 in the bauxite mines.

Besides the other test procedures sometimes the polarographic methods are also needed e.g. for the determination of Zn, Mo, Ga in different solutions.

In addition the LECO quick analyzer is successfully used for the determination of C and S in the aluminas.

From the above mentioned the wide-range application of analytical-chemical and chemical-physical methods can be seen in the alumina industry.

The exact course of the concrete analysis of the individual samples will be dealt with in the following chapters.

3. MAIN INSTRUMENTS AND ANALYTICAL METHODS

In the previous chapter a short description has been given about the most important conventional wet analytical and instrumental methods used in the alumina production according to Bayer. In this chapter a detailed description of those instruments and methods will be given which on basis of their wide measuring range and rapid operation are also useful for the automated checking of plant operation. These instruments which recently can be found in each alumina plant are as follows:

1. Emission Spectrum Analyzers
2. X-ray Spectrometers
3. Atomic Absorption Spectrometers
4. Instruments used for thermometric measurements (e.g. Aluminathermoquant)
5. Electroanalytical Instruments.

EMISSION SPECTRUM ANALYZERS

From the mid-thirties the optical emission spectrum analyzers came into general use in the aluminium smelters for metal analyses. Their area of application has been gradually extended on the materials of the alumina industry primarily alumina, then bauxite and red mud. The main difficulty with these samples is their non-conductive character in contrast to metals, thus their excitation is highly circumstantial.

Operation of the Emission Spectrum Analyzers (1,2)

It is well known that the excited atoms are emitting definite light radiation characterising only the atom in question, which can be observed by means of optical resolving system - the spectrograph and spectrometer - in the form of spectrum. The basis of the quantitative spectrum analysis is supplyed by the fact that the atomically excited elements are emitting line spectrum characteristic any time of their material quality. The corresponding spectral lines are compiled in charts in the literature (1).

Quantitative tests are based on the fact that the more atoms of the element in question are present in the light source the higher the intensity of the spectral line of a certain element is. From the radiation intensity of the spectral lines quantitative chemical counclusions can be drawn (2).

The quantitative evaluation is carried out by means of the reference standards.

With the spectral analysis first the atoms have to be excited; this can be made in case of the products of the alumina industry by a direct or alternative current arc generation, furthermore, low-voltage spark generation and recently by ICP.

The spectral analyzers can be divided into two groups.

1. Spectrographs by the use of which the spectrum resolved according to the wavelength is fixed on a light-sensitive emulsion. After the development the intensity of the spectral line is measured by means of the photometer.
2. Spectrometers by the use of which the line intensities are measured by appropriately set photomultipliers and accessory electronical measuring units.

Sample preparation

For the spectral analysis solid, powdered, conductive, non-conductive and liquid samples may be used. Since by means of this method usually small amounts of materials are tested special care should be taken of the homogeneity of the samples. Apart from the rapidity and high automation capability of the spectral analysis the main advantage of it is that small amounts of materials can also be tested.

Measurement

The selection of excitation procedures and the term of exposure required varies according to the type of the sample and components to be analyzed.

Evaluation

When following the quantitative evaluation the ratio of the intensity of the analyzing pairs of lines is determined on the basis of their blackening and after that the composition is generally determined by using approbate standards (wet chemically analyzed or weighed ones) prepared by similar ways.

The error of the spectral analysis by spectrographs is due to the emulsion and the error of photometry. This can be generally maintained at a level of 5 %. In case of spectrometers the error is generally less.

X-RAY SPECTROMETERS

X-ray spectrometers applicable in a wide measuring range (100 to 0.001 %) for the testing of elements ranging from fluorine (atomic number 9) to uranium (atomic number 92) came into general use in the last years in the alumina industry. This is partly due to the great development of the sensitivity and automated condition of X-ray spectrometers available and partly due to the fact that the sample preparation and calibration has been solved for most of the products (bauxite, red mud, alumina) in the alumina production.

The working principle of the X-ray spectrometers (indicated in Fig.3.1) is as follows: the sample is placed into the spectrometer and the elements of the sample are excited by the radiation of the X-ray tube to emit their characteristic radiation; then the fluorescent X-ray radiation is resolved by the analyzer crystal into its spectrum. The characteristic radiation is measured by a counter placed on the goniometer set at an angle of 2θ that corresponds to the individual elements (3).

In the irradiated homogeneous sample the concentration and the measured intensity may be expressed by the following equation:

$$C_i = R_i \cdot F_i \tag{1}$$

were: C_i the relative concentration of fluorescent element i
R_i the corresponding relative fluorescent intensity
F_i the interelement effect correction factor

Since R_i represents the fluorescent intensity related to the pure element i and since F_i represents the effect on the element to be measured caused by the other elements present in the sample the X-ray fluorescent method is not an absolute one and can only be practicable if evaluation based on chemically analyzed or prepared standard samples is parallelly made.

Sample Preparation

Two kinds of methods can be used for sample preparation depending on the nature of the sample and the quality and quantity of elements to be determined:

1. Powdered, homogenized, pressed specimens
2. Flux fusion (bead preparation)

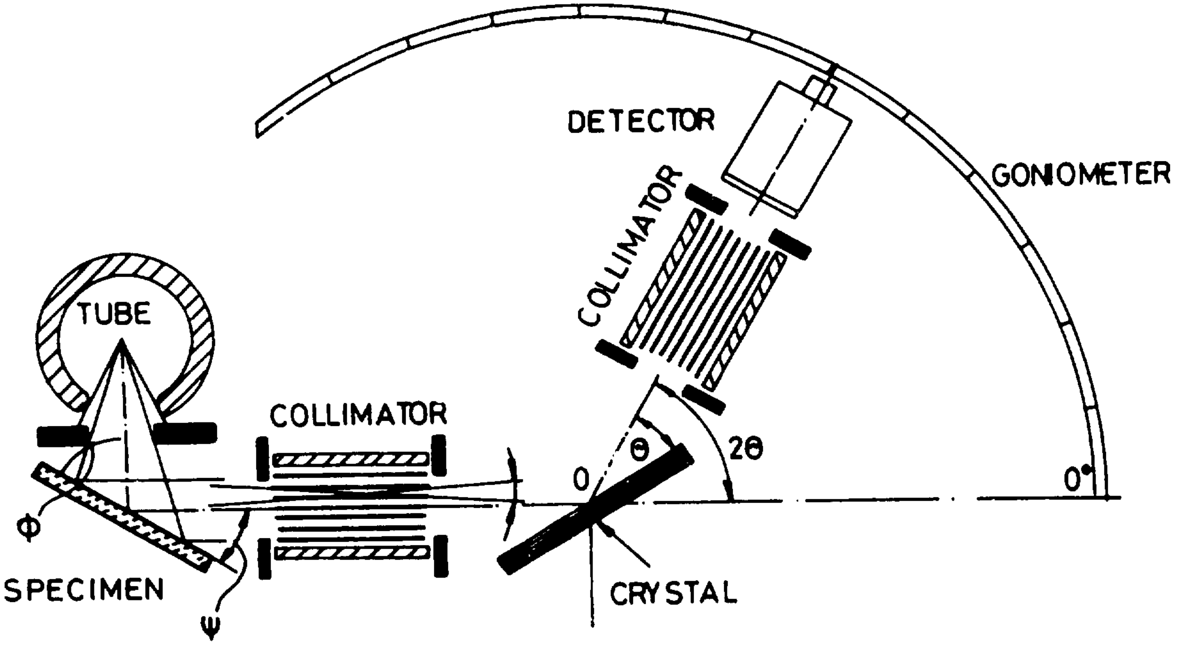


Fig. 3.1

ARRANGEMENT OF THE NONFOCUSING FLAT-CRYSTAL X-RAY SPECTROGRAPH

At first properly powdered (to - 30 µm) and homogenized, pressed samplex had been tested. This method, however, proved to be adequate only for testing alumina where the impurities of the order of 0.1 to 0.001 % besides the main component of Al_2O_3 could be fairly determined from the pressed tablets. In such cases it is expedient to carry out the test directly from the original material to avoid the dilution of the minor impurities.

This method did not prove to be adequate for the case of bauxite and red mud because very poor accuracy could be achieved due to the mineralogical composition and grain size of the samples and the interelement effect. The effect of grain size and mineralogical composition can be eliminated by the flux fusion, (with $Na_2B_4O_7$ and $Li_2B_4O_7$, resp.) the so-called bead preparation (4,5).

For the fusion high frequency induction furnaces are used where the fusion time is very short, 2 to 3 minutes or so. It is expedient to carry out fusion in an Au-alloyed platinum crucible because its wall does not become wettened by the melt during fusion thus enabling the melt to be completely discharged from the crucible. The test is performed on the homogeneous beads prepared this way.

Measurement

For the excitation of samples of the alumina industry it is advisable to apply an X-ray tube with Cr target because this is the most efficient method used for the excitation of elements of atomic number less than 23.

Evaluation

Since the X-ray fluorescent method is not an absolute one proper standard samples are required for the evaluation of the test results. The standards are carefully analyzed samples (e.g.

bauxite, red mud, alumina), however, good use can also be made of standard samples composed of oxides weighed together.

Sample preparation in this case has to be performed by the mode similar to that one in case of samples to be determined.

The composition of the standards should closely approach those of the samples to be tested, because in this case the matrix effect respectively the interelement effect can sometimes be neglected ($F_i = 1$). If multi-component - varying the concentration of the components within wide limits - samples e.g. bauxite, red mud are tested, the interelement effect is not negligible but it should be taken into account by applying either empirical, or mathematical corrections.

The most advanced applicable form for the practical evaluation is the self-consistent calibration method outlined by Tertian (4).

According to this the calibration has to be performed as follows: the oxides of the element to be measured should be added one by one to the sample used as a basis of calibration the latter containing all the elements to be determined. E.g. for the calibration of a system having, x number of components x + 1 samples are required, the standard and standard + x component addition and all the samples are measured for the intensities of all of the elements and thus the mutual effect of the individual elements is calculated. This method applies to calcined and to raw bauxites as well. For further details see literature (4).

An error of the X-ray spectrometric methods expressed as the standard deviation is 1 to 3 % relative error depending mainly on the sample preparation, out of which the instrumental error does not exceed 1 %.

ATOMIC ABSORPTION EQUIPMENTS

The AAS analytical technique developed in last years of the fifties has been introduced in the alumina industry quite rapidly for its relatively low expenses and simple sample preparation (in some cases solutions of sample can be used directly without any other procedure). This technique can be applied mainly if analytical problems need complicated procedures. (i.e. determination of Mg, Zn, Na, etc.).

Working Principle of the AAS Units (6,7)

A component present at a given concentration in the solution is excited to the atomic state by thermal energy. The atomic vapour depending on the concentration of the component will absorb the resonant frequency light of the light source. The wavelength of the light absorbed is characteristic of the quality of the component, its intensity, however, is proportional to its amount (concentration).

The AAS method is not an absolute one so the light absorption of suitably prepared reference solutions is compared. Since the resonant light source provides the resonant lines of a single element, in general, this is not a multi-element measuring method. Due to the small number of resonant lines spectral interference has to be considered only rarely.

The AAS-equipment consists of an atomizing unit, the resonant radiation source, light dispersion part and a light intensity meter.

The task of the nebulizing and atomizing unit is to produce atomic vapour proportional to the concentration of the component to be measured. For this purpose special gas burner and atomizing systems or electrically heated metal ribbon or graphite tube is used. The AAS-equipment is generally supplied with gas burner atomizing system. Apart from the viscosity of the solution to be tested and material quality of component and matrix to be measured the efficiency of atomization additionally depends on the design of the atomizer, the rate of atomization, the temperature depending on the chemical composition of the flame and the character of the flow of the flame (construction and shape of the burner head). The atomizing gas burner system is of decisive importance concerning the accuracy of the measurement.

Of the electrothermic atomizer (ETA) equipment the heated graphite tube has become mostly widespread. The ETA-system is generally used for trace analyses. Its further advantage is that small amounts of material are required.

As light sources the hollow-cathode lamps are generally used. For certain elements higher sensitivity can be achieved when applying electrodeless discharge lamps (EDL).

With the modern equipments using modulation of the heating current (also as a consequence of the separation of light (absorption and emission) long life (about 2,000 working hours) can be achieved. In the AAS-units normally 3 to 6 lamp-holders are provided.

A double-beam optical system serves as a light-detecting unit. Corresponding to the ultra-violet and visible range of wavelengths, furthermore, the thermal stress optical systems are used which are built-up of quartz or quartz-lined units having good resolution power (dispersion of 3 to 4 nm/mm). For the correction of the background radiation a deuterium lamp is normally installed.

The measurement of light intensity is performed with a photomultiplier. Modern devices, in general, provide digital display for the extinction and enable auto-zero setting and measurement under various integration times. Direct electronical display of concentration and curve correction possibility required from time to time is also ensured. The AAS-units can also be used in emission (as flame photometers).

Sample Preparation

By means of the AAS-units normally only solutions of the samples can be analyzed. Therefore most of the samples of the alumina industry have to be digested or dissolved prior to the investigation. For this purpose high-capacity target units (automatic digesters) are available.

For testing large quantities of samples now automatic sample changers are expediently used.

Measurement

The solution of adequately prepared samples are atomized in the burner head by the use of different gas streams depending on the component to be tested. Gas mixtures most frequently used for the investigation are: air/acetylene, and N_2O/acetylene, respectively.

Evaluation

The evaluation is carried out by a calibration curve plotted according to the extinction and concentration of reference solutions prepared similarly to that of the sample or by the standard addition.

The sensitivity of the AAS-method is 1 to 100 ppm (due to the preparation of solutions) when using flame-atomizing unit.

The error of the method is generally 1 to 5 % relative error when using flame-atomizing unit. When using electrothermic atomizer, however, it comes to 5 to 10 %.

THERMOMETRIC ANALYZERS

An instrumented laboratory control method, especially for the measurement of high concentrations is the thermometric concentration measurement. Simultaneously with the chemical (and phisical) changes heat effects appear which - in chemical reaction - are proportional with concentration. The direct thermometric concentration measurement started with the activities of H.J. Howard. (8)
In Hungary I. Sajó was the first to develop rapid thermometric (9) methods. In the past 15 years I. Sajó and his co-workers have developed a thermometric analyzer "Dithermanal" and for the alumina industry a specialized type the "Aluminathermoquant".

Principle of the Measurement

Direct thermometric concentration measurement is based on the exact measurement of the change of temperature which accompanies chemical reactions:

$$N_m \cdot Q_m = C \cdot \Delta T \qquad (2)$$

N_m = the amount of the component to be measured, in moles
Q_m = the molar heat of reaction, Kcal/mol
C = the heat capacity of the system, Kcal/C
T = the change of temperature in the system, ^{o}C

From the equation (2) the amount of the component in question is

$$N_m = \frac{C}{Q_m} \cdot \Delta T \tag{3}$$

and in molar concentration

$$c_m = \frac{N_m}{V} = \frac{C}{Q_m \cdot V} \cdot \Delta T \tag{4}$$

V = the volume of the solution.
If the value of the factor $\frac{C}{Q_m \cdot V}$ is held constant during the measurement by a suitable selection of the conditions of measurement equation (4) can be written as

$$c_m = K \cdot \Delta T \tag{5}$$

Equation (5) naturally remains valid if another concentration is introduced instead of the molar concentration.

Description of the Measuring Instrument

The exact measurement of the change of temperature is possible if two thermistor bridges are operated in a difference circuit. The temperature of the two measuring cells of indentical construction changes equally in principle due to the effect of the environment. Actually, however, one cannot produce two measuring cells with completely identical thermal insulation and heat capacity. Therefore, in spite of the difference circuit, a slight unidirectional change of temperature is observed in the system (2 to 5 minutes) the change of the temperature is practically linear for a short period and can be compensated electronically in a simple fashion. Figure 3.2 shows the sketch of the measuring instrument.

These measuring instruments can measure the changes of temperature which occur during chemical reactions with an error of less than $\pm 1.10^{-3} - 2.10^{-4}$ °C.

The construction of the instrument permits an indication of the amount of the component in question directly in g/l or %, after the insertion of suitable shunts and the transformation of the thermal effect into an electric signal.

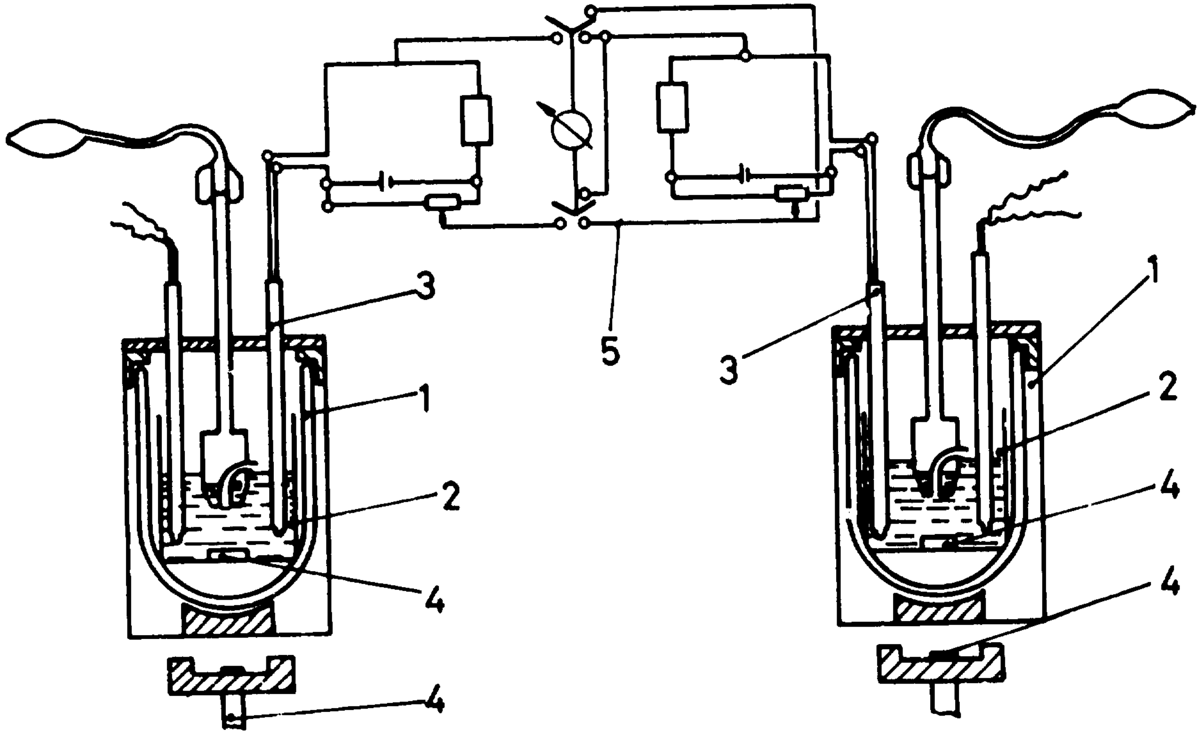
Sample Preparation

For purpose of the thermometric analysis liquid samples, solutions can be used.

Thermometric Measurement

Selective and specific chemical reactions are used for the measurement of the various components.

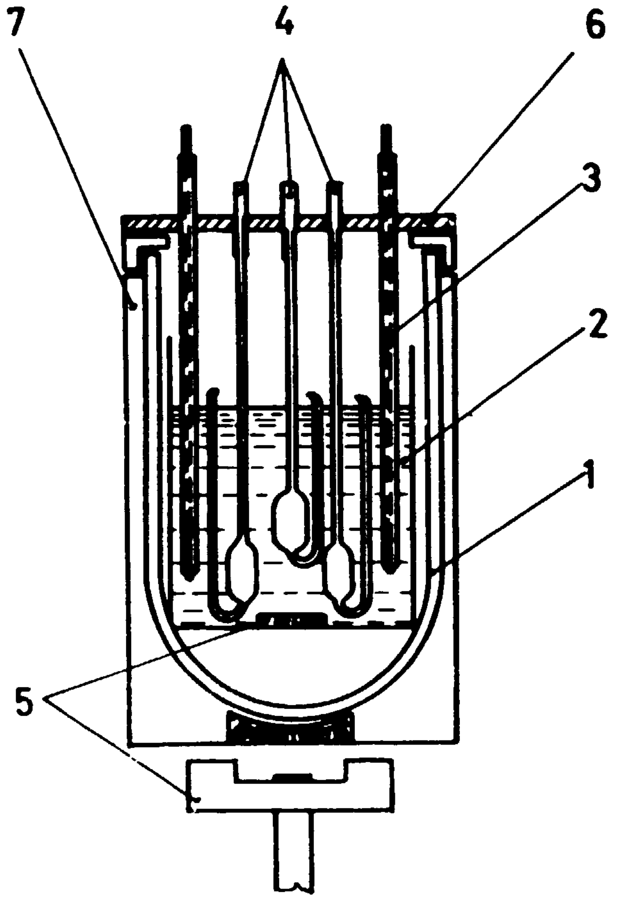
After suitable preparation of the sample its solution is placed in the measuring cell. (see fig. 3.3). After the establishment of the thermal equilibrium the reagent is added from a pipette introduced into the solution.
The instruments are calibrated by analyzing standard samples with conditions which assure the constancy of the member $\frac{C}{Q_m \cdot V}$ in equation (4) both during calibration and during the analysis of the unknown samples.
Thermometric analysis can be carried out rapidly with the precision of the classical analytical methods.



1. DEWAR FLASKS
2. PLASTIC BEAKERS CONTAINING THE SOLUTION
3. TEMPERATURE SENSING THERMISTORS
4. MAGNETIC STIRRERS
5. THERMISTOR BRIDGE SYSTEM

Fig. 3.2

SKETCH OF THE THERMOMETRIC ANALYZER



1. DEWAR FLASK
2. PLASTIC BEAKER
3. THERMISTOR
4. PIPETTES WITH REAGENTS
5. MAGNETIC STIRRER
6. CELL COVER
7. CALORIFER

Fig. 3.3

MEASURING CELL OF THE INSTRUMENT

ELECTRO-ANALYTICAL INSTRUMENTS

The electro-analytical techniques can be divided into three main groups: equilibrium and dynamic measuring methods, as well as those making use of the conductivity of ions.

With the equilibrium measurements the electromotive force is measured in currentless state (potentiometry), with the dynamic measurements the "electron" as a universal reagent is used so that current is constantly maintained to flow through the measuring cell (voltametry, polarography). When measuring the conductivity the transport of ions is measured on the basis of their electric conductivity (conductometry, oscillometry).

On the basis of the above the electro-analytical instruments can be divided into three groups, too.

Measuring Instruments of Potentiometry (10)

This is a high input resistance voltmeter and a measuring cell which consists of reference and indicator electrodes. Recently ion-selective electrodes are widely used for the measurement of different ion-activites.

Voltammetry, Polarography (11)

The modern polarographs, in general, consist of a potentiostat as a voltage source, a control signal generator required for the production of polarization voltage signals and the compensograph, respectively oscilloscope necessary for the measurement of the current. For coulometric measurements a current integrator is also needed.

The measuring cell consists of a working electrode (mercury or solid electrode), a reference electrode and a counter-electrode.

Conductivity Measurement (12) is commonly carried out by a 1.000 Hz frequency measuring bridge.

For oscillometric measurements electrodeless inductive or capacitive measuring cell is used. Oscillometric measurements have an important role in rapid control of the technological process. For instance, from the conductivity and density of the aluminate liquors caustic Na_2O, total Na_2O and Al_2O_3-content of those can be determined (13).

In addition to the instruments enumerated here, the alumina plant's laboratories possess wet analytical sections, too. Constituents of the wet laboratories are: photometers, spectrophotometers, titrimeters and other instruments. Working principle of the spectrophotometers is well-known thus some literature is referred only to (14,15).

It is only the quick analyser utilizing the neutron activation or X-ray fluorescent measuring method - the instrument used in the alumina industry - which have not been mentioned jet. It will be discussed later under the paragraph dealing with the individual types of samples (e.g. description of automatic bauxite analyzer (BEA) in Chapter 7.)

4. SAMPLING FOR CHEMICAL ANALYSIS. SOLID AND LIQUID SAMPLES, AVERAGING, SAMPLE VOLUME

The sample represents part of the material to be tested with the purpose to give information about one or more properties of the entire amount of the material.

Consequently the composition of the sample - at least within certain limits of error - must be identical with the entire material it was taken from.

For statistical calculations relative to sampling see the technical literature (16).

The mode of sampling is generally put down in standard specifications (17), however, certain deviations may also occur, the basis of which could be either a well established experience or a trade contract, too.

The sampling technique established in a processing plant or the sampling activity required in the course of the research work should also be included here.

Furthermore the random test is also frequently performed.

The task of the technologist is the processing of the bauxite deposit samples collected for him and sending them for further analytical and other tests. These samples should be handled as representative samples. The other samples occur in the course of the bauxite processing technology (red mud, aluminate liquors, alumina hydrate, alumina).

The samples are solids or liquors as regards the state of matter, or the mixture of the above ones i.e. slurries (red mud slurry, alumina hydrate slurry). The three kinds of samples have to be prepared for the chemical analysis by different ways. Primary aspect is that the sample should reserve its representative character.

PROCESSING OF SOLID SAMPLES

Solids are mostly lumpy with various grain sizes, heterogeneous the latter condition being frequently the function of the grain size. During movement and transportation the material can also be size-graded.

The material received must be homogenized prior to sampling. This is frequently difficult if the amount is little and big lumps are in it. In this case a comminution is necessary previously. For the extent of comminution it should be accepted as a directive that any heap of material could first be processed as a sample if the weight of its biggest lump is less than 1/1.000 to 1/3.000 of the weight of the bulk. This is a very strict precondition, if it is disregarded the sample can loose its representative character.

For information Fig.3.4 indicates the weight of the biggest permissible individual particle corresponding to the weight of any weights of a given heap of material in the course of homogenization. (This condition is advisable to be checked by screening and measurement.)

Only a certain portion of the material received or extracted for testing will become the sample. There are several reasons for this fact; it is expedient to reserve part of the material in its original state so cost and time required for sample preparation can be reduced and no surplus material is stored.

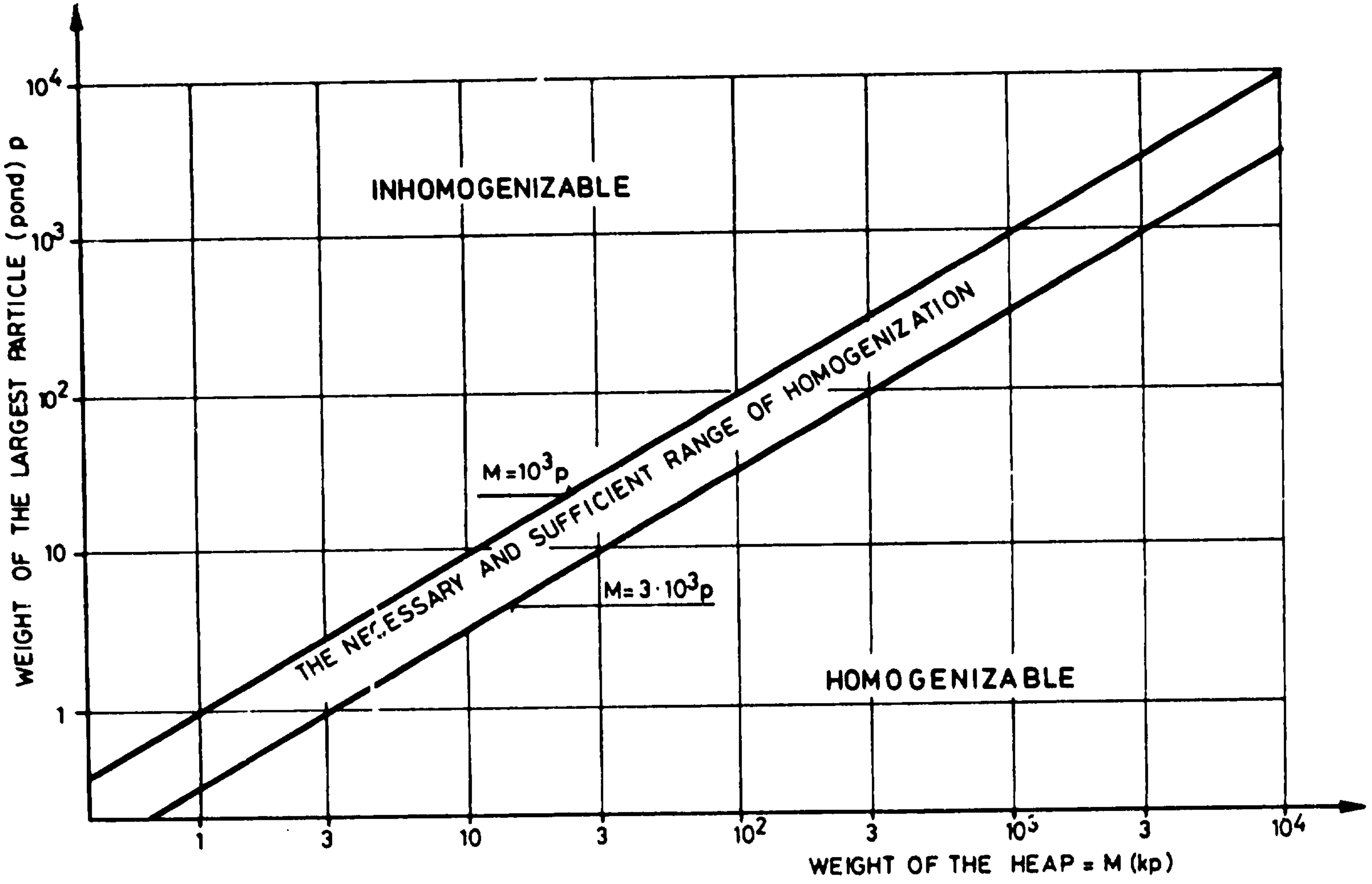


Fig.3.4

PRECONDITION OF THE HOMOGENIZATION

Based on the above consideration, the amount of material should be quartered. The reduction is always preceded by a comminution and homogenizing procedure i.e. the averaging. Comminution should be continued as long as the state of

$$10^3 p \leqq M \leqq 3 \,.\, 10^3 p \tag{6}$$

is achieved.

p = the weight of the biggest particle

M = the weight of heap to be reduced.

The reduction of the sample is made according to a convergent geometrical progression,

$$M_i = M \,.\, q^{n-1} \tag{7}$$

M = the weight of heap to be reduced

q = 0,5

In practice instead of the circumstantial weighting satisfactory results are also obtained by means of screening.

If the entire amount of material can pass through the screen of a given mesh the stipulation under equ. 6 is satisfied.

The relation between the weight of the particle and its diameter(d) can be calculated with the knowledge of the approximate specific gravity (γ) of the matter. It will not be a mistake if the shape of the particle is assumed to be spherical:

$$p = 0{,}524\, d^3 \gamma \tag{8}$$

p = the weight of the biggest particle
γ = approximate specific weight of the matter.

The weight of materials of various specific gravity are plotted against the particle diameter in Fig. 3.5.

Now the suitable set of screens has to be selected in order to have particles corresponding to the subsequent weights of p, 1/2 p, 1/4 p, etc., passing through it.

The standard scrren scales are generally designed on the basis of the $\sqrt[4]{2}$ aperture ratio e.g. Tyler Std.Screen Scale (18). Thus the amount of the sample can be reduced to its 1/4th volume by a single screening step. Every second member of the screen scale is used for checking the grain size.

For testing bauxite and red mud the 100 μm size or even less is generally used.

The mode of sample preparation required for the various instrumental and wet tests will be outlined there.

SAMPLING FROM LIQUORS

The liquor samples may be purely liquid phase or they may contain solids sometimes in considerable amount; the latter ones are the slurries.

The solid state samples occur either in the static or in the dynamic system. A storage tank, for instance, is considered as a static system and a production process, in turn, as a dynamic one.

The alumina production is a continuous process. The liquid phase (and the slurry) exists in dynamic balance (e.g. a prop-

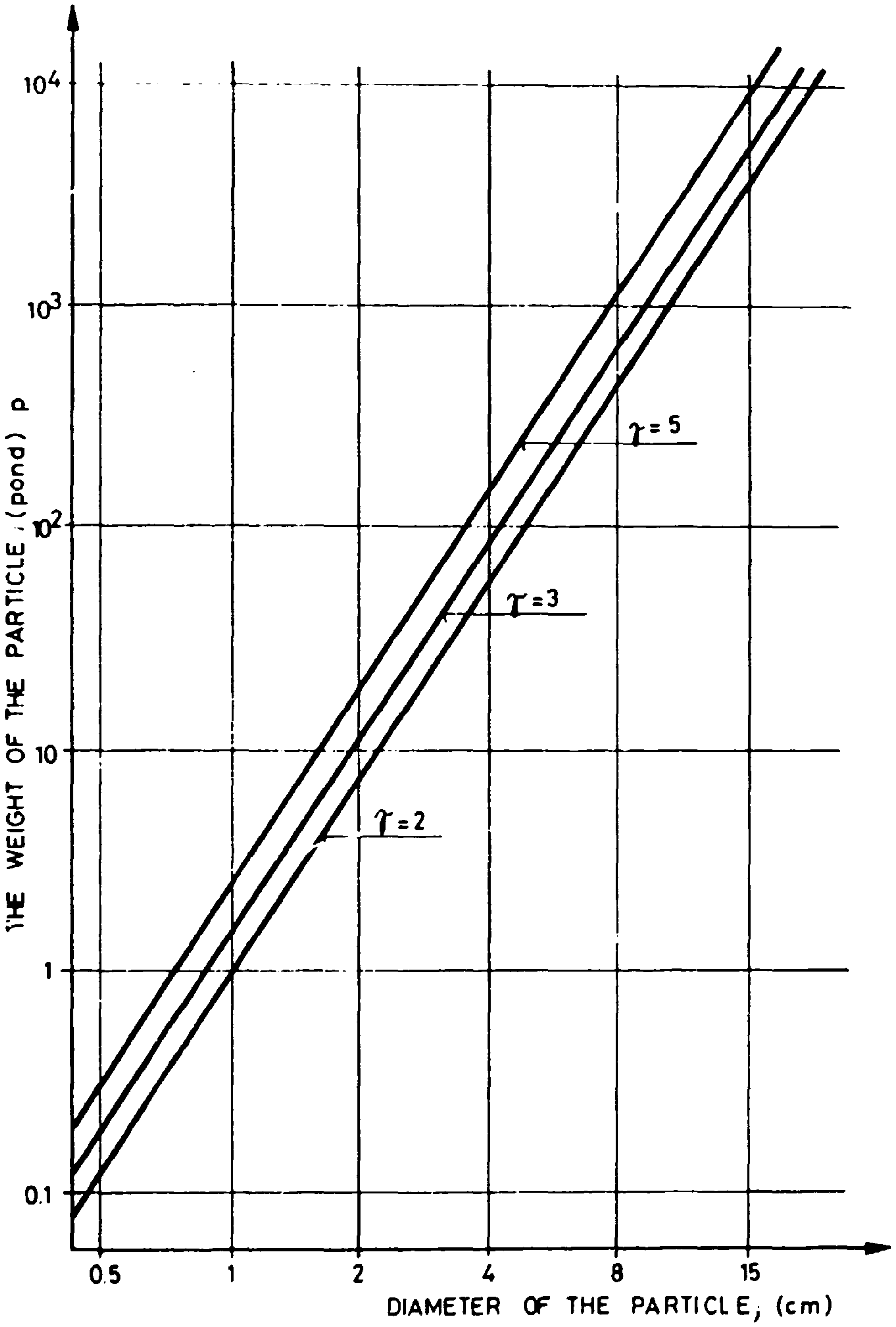


Fig. 3.5

THE WEIGHT OF THE PARTICLE IN THE FUNCTION OF PARTICLE DIAMETER erly running line of settler and washers) or in a metastable state (e.g. the batch precipitation).

The aim of sampling is to maintain the momentary state. If the sampling point is established and sufficient number of samples are taken within a given time interval the set of samples will be representative related to the process flow.

During the technological tests most frequently the static systems are met with. The sampling procedure is also simple as sometimes the entire amount of material may also constitute the sample. Inhomogeneity of the material represents significant source of errors when sampling liquors and slurries. Segregation according to specific weight and settling of solids from the slurries can be avoided only by careful and thorough stirring. This imperfection frequently occurs with the static systems.

In order to counterbalance momentary fluctuations for testing dynamic systems the "input" and "output" material flow has to be more frequently sampled.

When analyzing liquor samples - provided that they were extracted from a system of a metastable state - frequent troubles arise from the instability of the sample. The decomposition must be prevented by an appropriate method this may be either dilution, or the maintaining of an adequate temperature or simply the condition of carrying out the analysis before the sample starts decomposing. Anyway, the procedure preventing the decomposition should be satisfactory not to alter the representative character of the sample.

AVERAGING OF SAMPLE AND THE AMOUNT OF THE SAMPLE

Aim of the averaging of a sample is to provide suitable reduced amount of sample corresponding, however, to the composition of the large bulk of material.

The sample can become falsified by the shift in the ratio of the individual components in the course of quartering of the sample. The problems can be avoided by thoroughly homogenizing the sample by repeated rehandling or by the use of mechanized methods.

Similar source of error occurs with the technological test performed in the laboratory, e.g. solids can become classified after centrifuging.

Segregation or settling can also cause some errors with the liquor and slurry samples.

As a general rule, careful homogenization has to be performed prior to reduction or partition and analysis of samples. The time necessary for homogenizing the samples should be established experimentally. This can be easily done by the addition of some easily and accurately measurable tracing contaminants prior to homogenization of the sample.

The change of the amount of the tracing contaminant is determined from the samples taken from time to time will fairly indicate the homogeneity of the sample in the function of time.

The homogeneity of the powdered bauxite samples can thus easily be checked, i.e. by the addition of ZnO at a rate of 0.01 to 0.1 %. After leaching it with ammonium hydroxide it is measured by the polarographic method.

No figures generally valid for the amount of samples can be given.

It may be considered as guiding principle that it is advisable to keep 3.5 times the amount of material necessary for the entire test as sample.

Further aspects for the amount of samples could be the following:

- relevant standard specification
- agreement set up between parties
- necessity.

5. PROPERTIES OF BAUXITE, RED MUD AND ALUMINA FROM THE POINT OF VIEW OF CHEMICAL ANALYSIS

The bauxite is a raw material, the red mud is a waste product and the alumina is the final product.

The raw material bauxite is a rock; its geological criteria are described in Vol. 1, and its chemical composition can be seen in Table 3.1.

The chemical analysis provides information about the elementel composition of the material tested. The result of the analyses may be expressed in several terms. It is common with rocks and minerals that the components are expressed in terms of oxides. This is understandable because no simple and reliable method for the determination of oxygen in the analysis of minerals and rocks has been established up to now.

Anyway, this mode of expression should be used with reservation, because the composition expressed in oxides if formally used may be misleading, too. Therefore it should be thought over in each case separately which form to use for expressing the data and why to do so. As an example it can be mentioned that when summarizing the analytical data of calcite bearing bauxite the amount of CO_2 cannot be added to the other oxides because the former has already been covered by the figure of L.O.I. Neither the composition of pyrite (FeS_2) can be stated in the form of Fe_2O_3 and SO_3.

The composition of aqueous solutions and salts is expedient to be expressed in the ionic form ; by the comparison of the equivalent weights of the cations and anions the reliability of the analytical results can also be checked. In spite of the above mentioned the mode of expressing in terms of oxides is frequently used in the industry which is advantageous with tech-

Bauxite Main Components, Major Impurities, Trace Elements

Table 3.1

Main Components 0.5-60 %	Major Impurities 0.01-1 %	Trace elements 0.1-100 ppm
Al_2O_3	CaO	Ga
Fe_2O_3	MgO	Mo
SiO_2	Mn_3O_4 (MnO_2)	Zn
TiO_2	P_2O_5	Ni
H_2O	V_2O_5	Cu
	Cr_2O_3	Co
	F	As
	CO_2	Na
	C org.	K
	total $S \left\langle \begin{array}{l} S^{--} \\ SO_4^{--} \end{array} \right.$	R.E.*
	FeO	Pb
	ZrO_2	B
		etc.

* R.E.: Rare Earths

nological calculations, however, it could be a source of misunderstanding.

As an example the caustic Na_2O-content should be mentioned; it has little concern with the sodium, as actually OH-ions are measured!

The elemental composition is normally given for the analysis of alloys and organic compounds.

It can be seen from the above that the chemical analysis provides some information about the chemical composition of the material tested provided the possible modes of expressions are consciously used. The chemical composition itself is not always enough for the modern investigation, it has to be completed with other parameters, e.g. the mineral composition (see Vol.4.).

There are chemical analytical methods which may be considered as micro-technology. By means of those methods the analytical laboratory provides some more information for the technologist in addition to the chemical composition i.e. the extent of technological applicability-in certain relation-of the material tested.

Classical example of this is the so-called "pyrite sulfur" content in the sulfuric acid production or the "available CaO"-content of burnt lime.

Methods of this kind exist in the alumina industry, too; the determination of reactive SiO_2, non-reactive SiO_2, available Al_2O_3, causticisable Na_2O-content.

Of course, some parameters enumerated and used in the alumina industry depend on the adopted technology. The required parameters can be selected in the laboratory and by the use of the results of the precedential test quick information can be given to the technological laboratory.

As an example the sort of bauxite containing much quartz should be mentioned the silica content of which represents non-reactive SiO_2 when digesting at low temperature; the processing of the same by the high-temperature technology is no more economic.
Concerning the methods intended to be selected two properties of the sample should be taken into account from the point of view of the analytics:

- elemental composition
- mineralogical composition.

The elemental composition may vary within a wide range, thus an analytical procedure has to be selected by means of which the side by side determination of components present in the sample in a given ratio can be performed, so the matrix effects could be reduced to the minimum.

The mineralogical composition has a decisive role in the course of dissolving the sample: gibbsitic bauxites are acid soluble, the diasporic ones, however, can be dissolved only after being fused with alkaline substance before.

The same applies to red muds, too, and the same time the alumina plays a special role from this point of view (see p. 3-44). Effects of two properties of the sample in respect of the analysis are dealt with without aiming at completeness hereunder.

THE ROLE OF MINERAL COMPOSITION IN THE CHEMICAL ANALYSIS

The mineral composition affects the solubility of the sample. Several minerals have been detected in the bauxite, the conditions of solubility of those are highly diversified.

[illegible] bility is even more extended by the grade of [illegible] of the mineral in question and the micro-morphology [illegible]. It is well known that pyrite is difficult to get dissolved even in oxidizing acid mixtures. The high dispersity [illegible] content of certain bauxites can be dissolved, already in hydrochloric acid.

It is common rule for the dissolution that an amount of foreign material as high as by all means necessary should only be used for the dissolving of the sample in order not to increase the matrix effect superfluously. (It is well known that the analysis of pure materials, "typical specimens" always provides excellent results.)

The dissolution of a sample is nothing else than breaking of the crystal lattice; this requires input energy. Practically the time spent for breaking the crystal lattice i.e. reaction [illegible] is also an important factor. This can be increased by increasing the velocity of reaction i.e. elevating the temperature. The crystal lattice can collapse under the effect of heating and the incipient new phase shows more favourable character of solubility than the original one.

Thus the preconditions of the dissolution are given:

- transfer of energy (for the use of some sort of chemical reaction)
- increasing of velocity (increasing of temperature: boiling, heating, ignition)
- direct destruction of the crystal lattice (thermal cracking of the lattice to above the temperature of decomposition).

For the theory and practical performance of the same the technical literature is referred to (19), (20).

Depending on the mineral composition the bauxite and red mud samples are soluble in various solvents:

- in acids
- after thermal cracking in acids
- after alkaline-oxidizing shrinkage in acids
- after fusing with alkaline medium in acids
- after alkaline-oxidizing fusing in acids.

When dissolving the samples preference should be given to the methods by means of which the least amount of foreign substance is introduced to the system.

The dissolved sample is analyzed along with all substances used for the dissolution. The applicable analytical procedure depends on:

- the quantity of main components
- the ratio of main components
- the type and amount of solvents or fusing substances.

Whereas the determination of auxiliary components requires generally the application of special methods, trace elements, however, should at all times be determined in accordance with those described above.

The behaviour of the dissolved sample is described below.

THE FUNCTION OF COMPOSITION IN THE CHEMICAL ANALYSIS

As various kinds of possibilities for the chemical analyses are available, as many relations can be found between the amount of the component to be determined and the signal generated by the latter. Thus the component (x) to be determined may be described as a funciton (f) of a signal (s).

$$x = (f)s \tag{9}$$

This was the way how gravimetry, titrimetry and numerous other procedures based on functional relation had been developed.

A common feature of all the procedures is that the components in excess of those to be determined modify the signal to some extent. Distortion of the system can be caused either by the components of the samples themselves or the substances consciously added in the course of the analytical procedure. The first factor cannot be influenced because it is a given condition. The other factor can be kept at constant level and its effect can be taken into account.

Thus concerning the analysis the substantial interfering effect may arise because of the composition of the sample itself. The interfering effect (error) always occurs, but its degree is different i.e. it may be neglected for the practice or not.

The negligible error should not be considered, the somewhat higher, however, should be reduced to the acceptable level. The error can be diminished in two different ways:

- selection of a suitable method (functional relation) wherein the signal is not affected by the composition of the sample,
- removal of the component interfering with the signal by a suitable method from the system.

It ensues from the before-mentioned that for the analysis of bauxite, red mud, alumina and every other material a method should be adopted which performs a distortion-free signal for the component intended to get measured, either

- without the separation of interfering components, or
- after the partial or complete separation of the interfering compounds.

The composition of bauxites and red muds varies within wide ranges. The summary of practically applicable methods is given in the function of sample composition.

The possibilities shown in Fig.3.6 may become nil in special cases; searching for methods better to use and the finding of these means the enrichment of the chemical analytical science.

The basic principle of the methods indicated in the figure has been discussed in detail under Chapter 2 and 3, respectively.

ALUMINA FROM THE POINT OF VIEW OF CHEMICAL ANALYSIS

From the point of view of analytical chemistry alumina substantially differs from bauxite and red mud previously dealt with because while the latter ones are multi-component materials alumina is a homogeneous one - considering the analytical aspect - containing Al_2O_3 usually more than 98 % and the occurring other elements are contaminants. Consequently it remains mainly the matrix effect of the Al_2O_3 that has to be reckoned with, and in most of the cases the interfering interaction of the contaminants can be neglected during the analysis.

The mode of chemical bond and mineralogical structure of the contaminants of the alumina is not known in all cases; that is why the contaminants are internationally calculated in terms of oxides. Major contaminants of the alumina manufactured according to the Bayer process are adhesive moisture, chemically bound water the latter to be determined at various temperatures as a loss of mass and finally the Na_2O-content. The order of magnitude comes to some decimals of percent. Other contaminants occurring in alumina (See Fig.3.7) are of the 0.1 to 500 ppm order of magnitude.

Alumina is fairly resistant chemically, at an atmospheric pressure it cannot be dissolved in bases and acids (except for concentrated phosphoric acid). Therefore, at the analytical

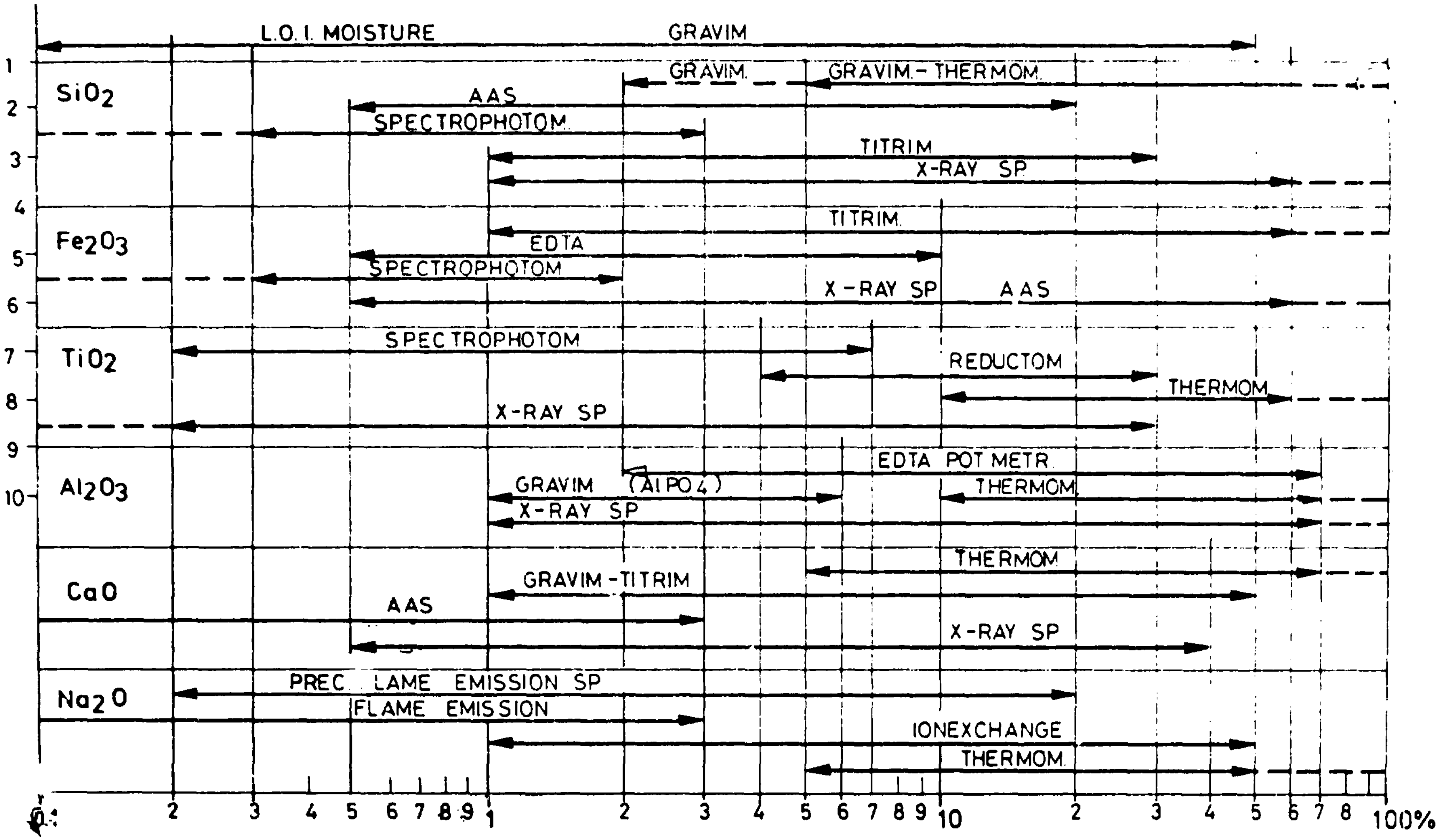


Fig. 3.6

METHODS FOR THE DETERMINATION OF THE MAIN COMPONENTS OF BAUXITE AND RED MUD

methods where the test is carried out [illegible] chemical analysis, flame-photometry, AAS, etc. The [illegible] and most laboursome procedure is the dissolution of the sample. One main precondition of proper dissolving lies in the adequate particle size of the sample the preparation of [illegible] a tough job due to the hardness (Mohs scale 9) of the alumina (αAl_2O_3). The sample preparation is described in detail [illegible] (Chapter 6).
Two methods are used for the dissolution of alumina:

- the alkaline fusion
- the attack by hydrochloric acid under pressure

Alkaline fusion is generally used prior to the wet chemical determinations. The samples of acid attack under pressure are very advantageous (low salt concentration) for the instrumental tests: spectral analysis in liquids, [illegible] AAS.

In some cases the selective leaching of contaminants occurring in alumina may also be used, e.g. the leaching of water soluble Na_2O-content or the leaching with ammonium carbonate for the determination of the sulfate content.

Consequently from the order of magnitude of the contaminants the wet analytical methods - mainly spectrophotometric procedures - are carried out from the stock solution made after fusion. In some cases the separation with a parallel enrichment may also be necessary (e.g. extraction [illegible] in the case of ZnO, or V_2O_5 and distillation separation in the case of F and B_2O_3). Since the fusion of alumina is a very laboursome and slow procedure spectral analysis or X-ray spectrometric methods are generally used for checking the process in the alumina plants. Due to the low concentration of contaminants the unjustified dilution of the sample [illegible] also be avoided.

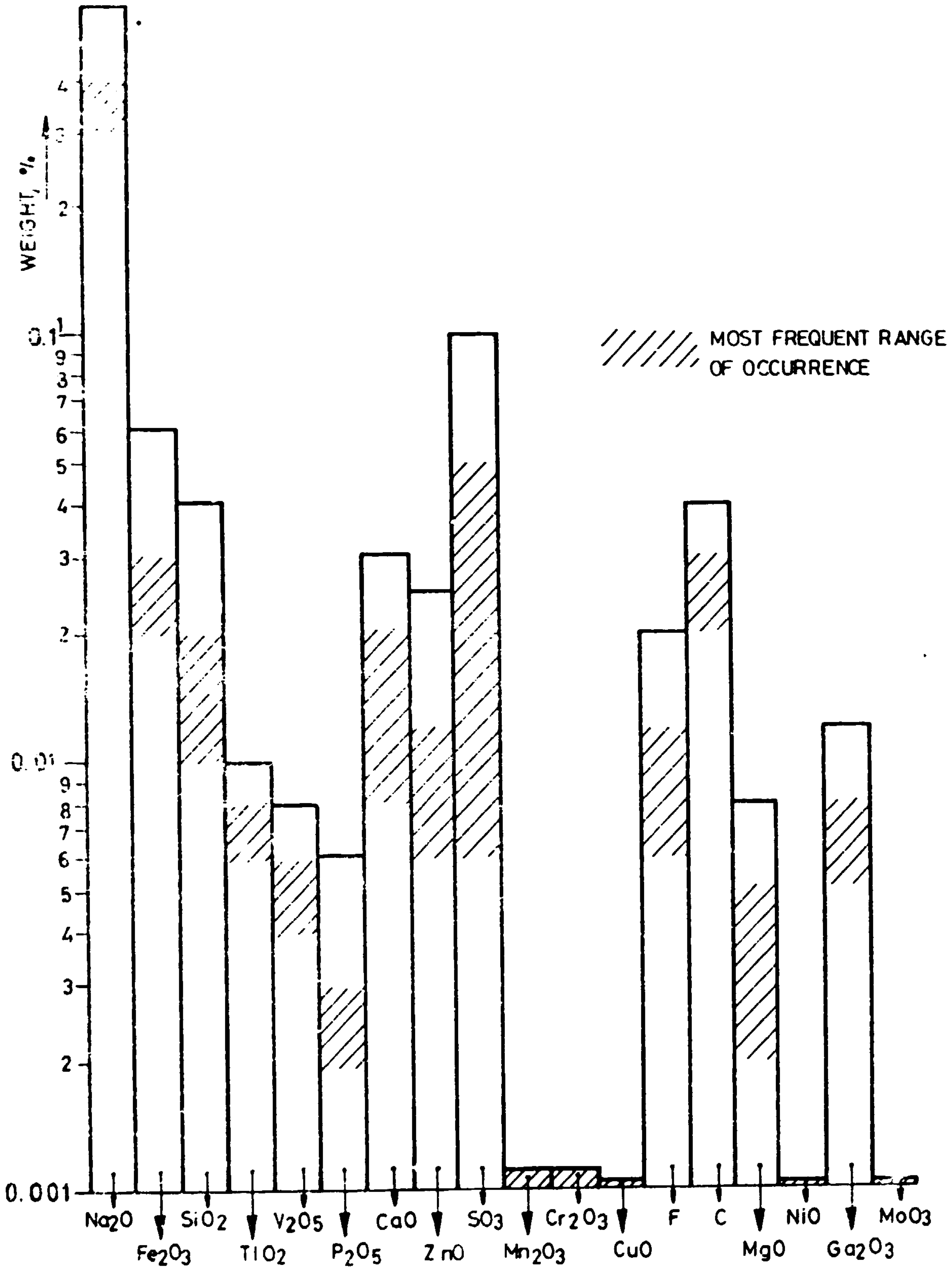


Fig. 3.7

CONTAMINATING COMPONENTS IN ALUMINA

6. PREPARATION OF BAUXITE, RED MUD AND ALUMINA FOR CHEMICAL ANALYSIS

The aim of the preparation is to make the sample taken from the bulk of material in question suitable for the chemical investigation.

The preparation starts already at the sampling when the material is crushed, its mass is reduced, dried if necessary and packed.

The samples of materials used and incipient in the course of alumina production comprise more or less amount of moisture. The amount of moisture should also be known therefore a separate sample has to be taken for the determination of moisture. This operation is not easy to carry out because the sample must not loose any of its original moisture content during the preparation. This is demonstrated by the condition that a separate "moisture sample" is generally taken which serves exclusively for the determination of moisture.
For the chemical investigation the sample resulting after quartering and averaging is used.

The sample used for chemical analysis is expected not to change its condition during transport and storage.

The sample may alter upon standing. The change may have a physical or chemical character; by adequate preparation those changes can be avoided or reduced to a negligible level. In the alumina industry primarily the change of moisture content has to be reckoned with. Minimum change in the state occurs if the sample is in equilibrium with its environment. For the purpose of chemical analysis and for the sake to ensure weight constancy the dried and adequately powdered sample should therefore be brought to equilibrium with the humidity of the environment. This is ensured by spreading the sample

in a thin layer for a considerable period, practically for a few hours.
With the testing of hydroscopic materials, for example, solid NaOH, the sample has to be isolated from its environment.

Other kinds of physical changes, for example recrystallization, do not play any role in the Bayer technology as regards the chemical analysis.

Chemical changes occur similarly under the effect of the environment. As an example it should be noted that at the drying operation of the causticized red mud the sample containing unreacted $Ca(OH)_2$ will fairly change the composition.

$Ca(OH)_2$ forms $CaCO_3$ under the effect of CO_2-content of the air, thus the original $Ca(OH)_2$ and CO_3^{--}-content of the sample cannot be determined, even more also the measurement of moisture content becomes illusory.

In order to avoid chemical changes the sample should be prepared so as to hinder respectively minimize the interfering chemical influence arising under the effect of the environment.
On the basis of the above it can be seen that the preparation of the sample has to be carried out in accordance with the objective aimed at.

When analysing red mud the relation of the SiO_2, Al_2O_3 and Na_2O-contents has to be determined, the sample may be dried since the chemical changes do not influence the above relations. If the amount of unreacted $Ca(OH)_2$ retained in the red mud has to be determined the sample should be protected from the CO_2-content of the air.

It belongs to the preparation as well that to what size the sample should be reduced to. No definite answer can be given in this concern. The velocity of dissolution is directly proportional to the increase of grade of dispersity of the sample. It ensues from this that samples slow to dissolve should be ground to finer grain size than those faster to dissolve.

It is a general experience that the hardness and the mechanical strength of the samples slower to dissolve is also higher thus the finer the grains are ground the more foreign contaminating material is worn off the grinding equipment.

Considering the above only a compromising solution can be found. The sample should be pulverized to a suitable grain size so as to achieve acceptably short time of dissolution at the chemical analysis and at the same time a minimum contamination due to the grinding apparatus.
Of course, the practical selection of the dissolution or digesting chemical process for the rapid dissolution of the sample is also at our disposal.
Practical figures for the grain size are as follows:

- for fairly soluble gibbsitic bauxites: 150 /um
- for mixed type gibbsitic-boehmitic bauxites and red muds: 100 /um
- for hard diasporic bauxites: 50 /um

In this case the samples fairly meet the analytical requirements. It is also important to remark that non-uniform breakage of the mineral grains of different hardness occurs during the pulverization. After pulverization the larger grains should be separated by sieving and further pulverized as long as the entire amount of sample passes the required mesh aperture. When screening the particles should pass by the action of shaking rather than rubbing or even by the use of a brush causing the contamination of the sample.

Packing of the sample represents the last phase of the sample preparation.

The sample should be placed into an adequate container or bottle, sealed air-tight. A label should be provided stating the neme of the material, place and date of origin, the amount of the sample, code number of the sample, possible special data and the signatures of the sampler and the dresser, respectively. Quite often happens that samples prepared for chemical analysis are received. The duly labelled and corked, possibly sealed sample guarantees the proper preparation and at the same time confines the responsiblity of the laboratory to within the good quality of the analytical work and not beyond it. It is proposed for the technological laboratory investigation that the technologist and the analyst should consult the aim of the investigation, about the suitable sample preparation and the performance of the analytical method to be applied.

International Standard Specification (ISO 2927-1973) specifies how to take the representative sample of alumina used mainly for the production of aluminium.
This contains detailed prescriptions for the sampling of alumina for the cases of

- transportation, loading
- unloading, storing and
- taking samples from the flow.

This standard specification establishes the amount of laboratory sample to be 500 g. The reduction of the bulk sample to this weight is carried out by means of quartering method, known for pulverized materials, as quickly as possible.

When sampling due care should be taken of the unchanged physical and chemical state of the alumina.

The particle grain-sizes range between a few micrometers to 300 /um. Therefore, the alumina should be ground and pulverized and screened untill all the material passes through the screen of mesh aperture 0.2 mm.
As already indicated (page 3-46) alumina is a very hard

material, it should be carefully ground because it can become contaminated by the construction material of the grinding mill or the mortar (e.g. when pulverizing in the agate mortar the SiO_2-content of the alumina increases). For the pulverization of alumina corundum mortar should only be used. Similarly by the use of the alundum mortar the alumina can become contaminated (particularly by CaO, MgO and SiO_2).

Care should be taken of the construction material of the screens the selection of which should be made depending on the contaminant to be determined.

Then 300 g of pulverized, screened and thoroughly mixed sample is placed into a suitable container (possibly platinum) and dried at 300 ± 10 °C for 2 hours. The sample is allowed to cool in a desiccator then it is placed into an air-tight container of such a capacity that it is nearly filled by the sample (21).
This sample is used for both the physical and chemical tests.
For the required labelling of the sample, see page 3-50.

7. DETERMINATION OF THE MAIN CHEMICAL COMPONENTS OF BAUXITES. COMPARISON OF DIFFERENT ANALYTICAL METHODS.

Main components of bauxite and their amount has already been indicated (see Table 3.1). Concerning the H_2O-content of the sample it should be additionally mentioned that it should be divided into three parts:

- moisture (water content of mined or delivered bauxite)
- adsorbed moisture (water content of sample dressed for the analysis and balanced with the humidity of the environment)
- structural water (chemically bound water content of the oxide-hydrates)

Theoretical concern of the determination methods of the individual main components are dealt with hereafter.

MOISTURE CONTENT

Moisture content of the mined ore is a characteristic feature not to be negligible. It causes excess costs on transportation, the costs are further increased in the alumina plant because the water content of bauxite dilutes the digesting liquor and this excess water has to be evaporated in evaporator sets by the use of expensive thermal energy.

Concerning quarry sap respectively the conditions of the moisture content of the bauxite cargo the relative standard specifications or the agreement set up between the Seller and the Purchaser will provide for. The measured "moisture content" rarely approaches the actual state, the results should be regarded as being conventional.

MOISTURE CONTENT OF THE AIR-DRY SAMPLE (ADSORBED MOISTURE)

First of all the attention should be drawn to a wrong aspect. The sample is dried before the analysis and the measuring lot is taken from this material. According to our measurements bauxite adsorbs considerable amount of moisture within a short time from the environment, which primarily falsifies the figure for L.O.I. and furthermore errors occur with the measurement of the main components, too. Red muds are even more hygroscopic than bauxites, thus the errors would increase. In order to justify our statement a figure is shown indicating the increase in the weight of a bauxite sample dried at 130 °C, then cooled to 25 °C in a desiccator and finally exposed to the open air (Fig.3.8).

The sample may pick up moisture to a few 0.1 %. Consequently, during the weighing procedure (1 to 2 minutes), by the time the lots for all the determinations are measured out a change in weight as high as 1 % could occur.

Therefore the measuring out of an air-dry sample balanced with the humidity of the environment is recommended. The dried sample may attain at the air-dry state within a 4 to 16 hours exposure to the open air.
Of course, the amount of adsorbed moisture content has to be measured. Its measure will be the loss in weight after having the sample dried. The temperature of drying is higher than 100 °C, accurate data can be achieved by the thermogravimetry only (see also Vol.5.)this may be approached by drying for 2 hours at 130 °C.

In the knowledge of the moisture content of the air-dry sample the data of the other analytical results should be transformed to the dry basis.

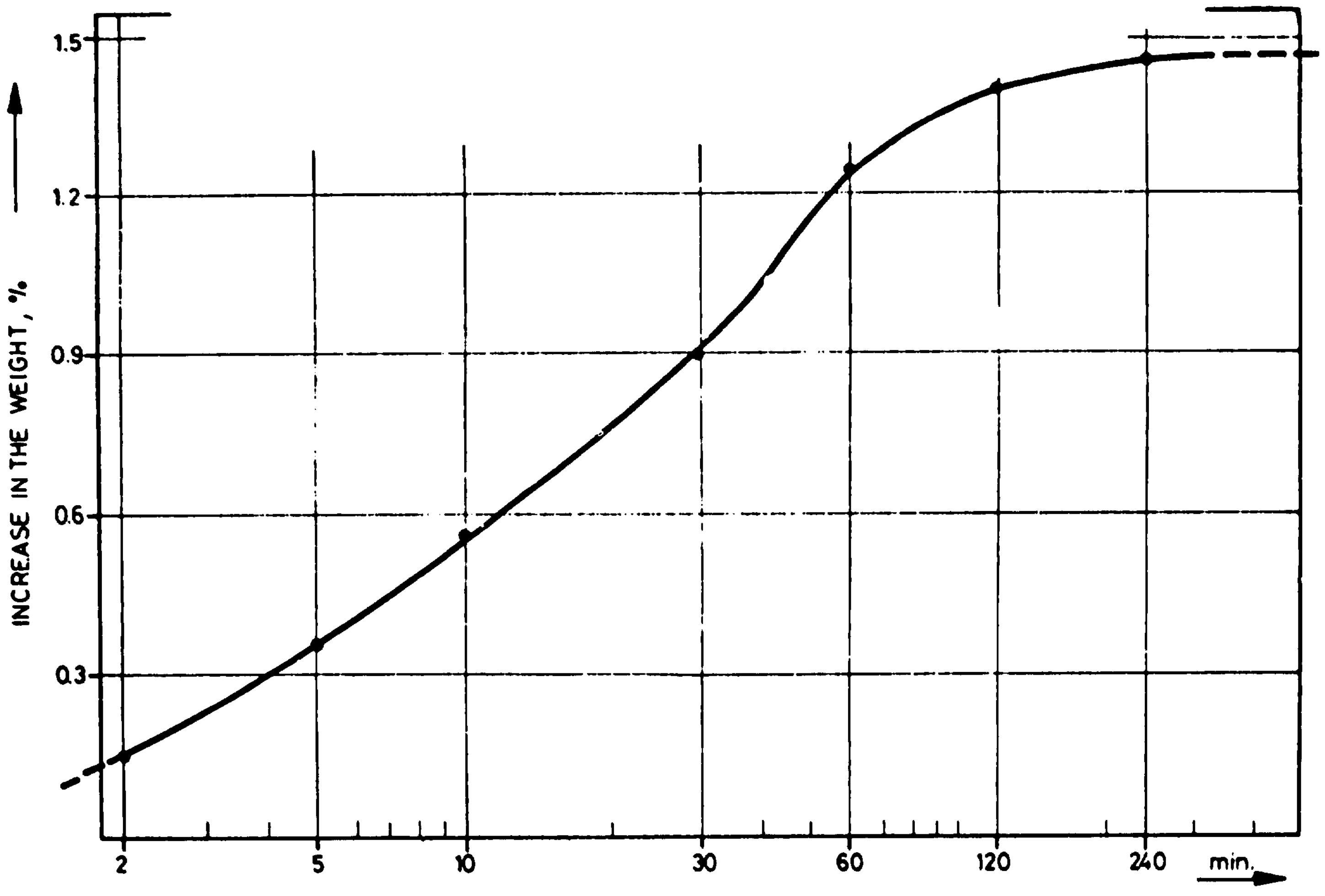


Fig.3.8

MOISTURE ADSORPTION OF THE DRIED BAUXITE

DETERMINATION OF LOSS ON IGNITION

The measurement of loss on ignition compensates more or less the so far lacking method for the measurement of the oxygen content. The amount of L.O.I. - after some consideration - may be used to decide the adequacy of the analysis upon. (The summary of measured components comes to 100 %).

During ignition structural changes take place in the bauxite and in the red mud. After having ignited at a given temperature the stable form of the mineral components is obtained.

A loss in weight can be commonly observed because the volatile components (H_2O, CO_2, etc.) are driven off. The increase in weight can be only the consequence of some kind of oxidation, this is, however, of secondary importance in the samples of the Bayer-type aluminium industry (e.g. pyritic bauxites). Related to the ignition temperature of the samples the treatment within the range of 1000 to 1100 °C is common. Reliable temperature data may be obtained by means of the thermogravimetric analysis (22).

There are different opinions concerning the period of ignition, we represent the point of view that those L.O.I. values which are in agreement with the thermogravimetry approach the actual value best.

Empiric data: ignition for 2 hours at 1050-1100 °C. Stable form of the individual components at the above temperature:

- H_2O - gets completely removed
- CO_2 - gets completely removed (even from red muds)
- organic substance - gets completely removed
- sulfur content (pyrite, sulfates) - gets removed to the highest degree. If large amounts of Ca are present it can be partly retained, so thermoanalytical

test should be carried out to clear up the conditions

- silicon - its stable form is SiO_2 even for its compounds
- aluminium - the stable form is Al_2O_3; this may also be hygroscopic when ignited for a short period
- iron - its stable form is Fe_2O_3, however, the presence of manganese can result in some proportion of Fe_3O_4, too. This error may be negligible.
- titanium - its stable form is TiO_2
- calcium - its stable form is CaO. If no suitable anions are available the ignited sample is hygroscopic and picks up CO_2, too, ($CaO + H_2O \rightarrow Ca(OH)_2$) and $CaO + CO_2 \rightarrow CaCO_3$), respectively
- sodium - this is the most sensitive component, because several compounds of it volatilize at higher temperatures. After having ignited losses have to be reckoned with. The error limits at the margin of the tolerance
- the other components by virtue of their share are of secondary importance.

DETERMINATION OF THE SiO_2-CONTENT

The SiO_2-content of bauxite represents a measure of value, thus its accurate determination is of vital importance.

The methods generally used for the measurement of SiO_2 are referred to in the technical literature:

- gravimetric (19)
- titrimetric
- spectrophotometric (23) method

Not everyone of the enumerated methods is suitable for the determination of the SiO_2-content of the bauxite.

In the course of the determination of SiO_2 one typically meets with the possiblities of the analytics and the require-

ments of the technology. The request is to be fast and accurate, the possibility, in turn, the slow and moderately accurate character of the methods. This relates, however, to the classical analyses only.
There are methods available, which enable the rapid and accurate analysis, however, with the use of expensive, and sensitive instruments.

If technological tests are made, the classical analysis or the fast analysis based on a classical principle yields good result.

The accurate measuring result is influenced by the incomplete dehydration of silica. The dehydration is difficult to be performed in the case of bauxites being difficult to digest, because the dehydration is less complete in the presence of alkali metals (the compounds of the digesting substances).

There are several possibilities for solving the problem:

- duplicate predesilication of the silica
- single predesilication of silica, then spectrophotometric measurement of dissolved SiO_2 in the filtrate and application of experimental correction
- with samples of identic feature a single predesilication of silica and empiric correction
- measurement by the AAS method and calibration against a reliable standard sample
- fast analytical method - reliable standard samples.

If no high accuracy is intended to be achieved when measuring the SiO_2-content of the bauxite an absolute error ranging 0.15-0.6 % can be taken into consideration.

There are bauxites available which contain SiO_2 less than 1 %. The classical gravimetry can not be applied with their analysis, it is expedient to apply here the spectrophotometric measurement.

Larger amounts of SiO_2 can be also analyzed by spectrophotometry. By an adequate spectrophotometer even 40 % of SiO_2 can be accurately determined.

The question of reactive and non-reactive SiO_2-content is frequently raised from the point of view of technology.

If the sample is acid soluble the non-reactive quartz remains undissolved along with the silica-gel precipitating from other SiO_2 compounds. Diluted hydrogen fluoride solution dissolves the latter within a few minutes whereas quartz hardly dissolves. After filtration and washing, it can be ignited and established so.

DETERMINATION OF THE Fe_2O_3-CONTENT

Iron is mainly represented in the bauxite in the form of FeIII, the FeII figures as a subordinate. From technological aspect the determination of the total iron content is essential. When analyzing bauxite the measurement of Fe_2O_3 is the easiest to perform, partly because none of the components interfere with its determination, partly because proper analytical methods are at our disposal.

Methods serving for the measurement of the Fe_2O_3-content:

- permanganometry (24)
- chromatometry (24)
- titanometry (24)
- ascorbinometry (24)
- complexometry (25)
- stannometry
- spectrophotometry (23)
- AAS

The determination of the FeII-content (26) requires much caution due to the interfering components and still the results are not much reliable.

DETERMINATION OF THE TiO_2-CONTENT

TiO_2 varies within a wide range (0.5-10 %) in the bauxites. The spectrophotometric method (27) used commonly yields acceptable results only below 5 %, in cases of higher TiO_2-content the differential-spectrophotometric method or the reductometric analysis (28) provides adequate result. Recently the thermometric method has also been proposed for the measurement of higher amounts of TiO_2.

Should any method be selected, the measuring error would not be reduced to below 0.1-0.3 abs.%.

DETERMINATION OF THE Al_2O_3-CONTENT

Apart from SiO_2 (and other detrimental materials to technology) the measure of the value of the bauxite is its Al_2O_3-content.

The determination of Al_2O_3 is one of the most difficult tasks of the analytical chemistry because several other components being present interfere with the accurate determination.
Earlier and for quick informative tests even nowadays the Al_2O_3-content is clacculated on the basis of the difference. Those results can, however, only be of an informative character.

There are numerous methods recommended for the determination of the Al_2O_3-content in the technical literature.

The interfering effect outlined under Chapter 5 can be noticed to the greatest extent at the determination of the Al_2O_3-content. Therefore most of the methods carrying out the determination of Al_2O_3 without the elimination of the interfering components yield faulty results. The error can amount to a few %.

A few methods are only available for the determination of the Al_2O_3-content of bauxites. Apart from the valid, however, not always proper standard specifications it is hard to find any references in the literature. The alumina plants processing bauxite are generally not publishing their analytical procedures.

The principle of three basic analytical methods are discussed below:

- complexometric titration without the separation of the interfering components,
- complexometric titration with the separation of the interfering components,
- potentiometric titration with partial separation of the interfering components.

Complexometric Titration Without the Separation of the Interfering Components

The principle of this method is that all the metal ions are converted into a complex form by excess EDTA solution (ethylene-diamino-tetraacetate) then the excess amount of complex-former is back-titrated by Zn^{2+} standard solution. Under the effect of fluoride ions the Fe-EDTA complex will not, however, the Ti-EDTA complex will rapidly decompose at room temperature. If now the excess amount of the EDTA solution is measured only the Al-EDTA complex is in dissolved state which when boiled will decompose under the effect of fluoride ions. After cooling the amount of EDTA equivalent to the Al_2O_3 can be measured.

Complexometric Titration With the Separation of the Interfering Components

The method described under page 3-60 will not supply accurate results with extreme TiO_2 to Al_2O_3 ratios. If the Fe_2O_3 to Al_2O_3 ratio is high, indication problems arise due to the solution's own colour.

The mentioned sources of error can be eliminated if the Al_2O_3-content of the R_2O_3 precipitate separated by hydrolysis is dissolved by NaOH. The loss of Al_2O_3 adsorbed on the precipitate residue may be taken into account by making corrections.

Potentiometric Titration (29)

The Al^{3+} ions in the filtrate of SiO_2 can be converted to aluminate by means of excess NaOH:

$$Al^{3+} + 4OH^{-} \rightarrow /\ Al(OH)_4\ /^{-} \qquad (10)$$

When neutralizing by acid solution to a given pH value $/Al(OH)_4/^{-}$ can be obtained.
Under the effect of KF the following reaction takes place:

$$/\ Al(OH_4)\ /^{-} + 6F^{-} \rightarrow AlF_6^{3-} + 4OH^{-} \qquad (11)$$

The OH^{-} equivalent to the Al_2O_3-content can be titrated.

Other ions of the solution do not interfere considerably, the error may be compensated by correction.

Utilisable Al_2O_3-Content

From the point of view of alumina production the amount of Al_2O_3 recoverable from bauxite is of importance. If the bauxite sample is treated with NaOH solution at a temperature corresponding to the technological parameters it gets digested. After filtration a solution containing little amount of silicate is obtained.

If its Al_2O_3 and SiO_2-content is determined an index-number of the available Al_2O_3-content is obtained.

$$Al_2O_3\ _{\text{available}} = Al_2O_3\ _{\text{total}} - 0.85\ SiO_2$$

INSTRUMENTAL TESTS MADE FOR THE DETERMINATION OF MAIN COMPONENTS OF BAUXITE

X-ray Spectrometry

As it was already mentioned under Chapter 3, the X-ray spectrometry is very good for the investigation of the main components of bauxite and excellent for carrying out fast series-analyses. Due to the influence of the mineral composition the examination of the main components of bauxite cannot be performed from the pulverized sample directly. Bauxite is ignited at 1100 °C and L.O.I. value is established.
Then it is fused with borax at a ratio of (1:9) (bead preparation). The parameters of the analysis are given in Table 3.2. Besides the main parameters (SiO_2, Fe_2O_3, Al_2O_3, TiO_2, , CaO can also be determined by this way if the latter exceeds 0.5 %. The evaluation is carried out by means of standard specimens composed of weighed-in aluminium oxide, iron III-oxide, silicon oxide, titanium oxide and calcium oxide compounds or by standard bauxite samples (4,30) analyzed by wet methods.

By means of this method SiO_2, TiO_2, Fe_2O_3 and Al_2O_3 content of bauxites can be determined by making relative error of maximum 2 %. The method is extremely fast. When using automatic bead preparation an amount of 20 to 100 samples can be analyzed in a day for 5 components. The automatic device enables overnight work, too. The sample preparation, i.e. reduction of grain size to minus 60 μm corresponding to the measurement, is the most laboursome procedure requiring due attention.

X-Ray Analysis of Bauxite
Working Conditions (Cr target) 55 kV/44 mA

Table 3.2

Component	Crystal	Meassuring instrument	Goniometer	Collimator
Al	PET*	Flow-Counter	145,10 °	Coarse
Si	PET	Flow-Counter	109,20 °	Coarse
Ti	LiF	Flow-Counter	86,10 °	Fine
Fe	LiF	Flow-Counter	113,20 °	Fine
Ca	LiF	Flow-Counter	37,30 °	Fine

* Pentaerythrite

Determination of Major Components of Bauxite by AAS (31)

The determination of the major components (Al_2O_3, Fe_2O_3, SiO_2, TiO_2, CaO, MgO; in the red mud Na_2O, too) of bauxite and red mud is one of the most important analytical tasks in an alumina production plant. As the base of AAS methods for different siliceous materials have been elaborated during the last decade its application can be promising on this field. A well developed and partly automated AAS system gives a very economic solution for these problems considering the proper accuracy and speed of the method.

Some methodological questions had to be solved for the proper operation, these are the elaboration of the most suitable sample preparation, the elimination of the matrix effects and the correction of the possible instability of the AAS instrument originating from the long time operation at a high temperature as N_2O - acetylene flame is used.

The bauxite and red mud samples were fused with the mixture of $SrCO_3$ - H_3BO_3 at 1000 ^{O}K temperature. The application of $SrCO_3$ as a flux eliminated the matrix effects, too, being a good ionization buffer.

The slight instability of the AAS instrument had to be corrected because of the high accuracy requirements. By the application of some (5-6) "set in" probes in a series of 50 samples and a computerized correction procedure this disturbing effect can be eliminated.

This AAS system can be applied for the analysis of bauxite and red mud samples for the mentioned 6 or 7 components. The variation coefficients for the different components are: Al_2O_3 1, Fe_2O_3 0,5, SiO_2 3, TiO_2 3, CaO 5, MgO 5, Na_2O 1.

Thermometry

In some cases the direct enthalpometry can be advantageously used for the analysis of bauxites.
The suggested selective chemical reactions for the determination of the main components of bauxite are as follows:

SiO_2:

$$SiF_6^{2-} + 2K^+ \xrightarrow{H^+} K_2SiF_6 \downarrow \qquad (12)$$

Fe_2O_3:

$$2Fe^{3+} + Sn^{2+} \xrightarrow{H^+} 2Fe^{2+} + Sn^{4+} \qquad (13)$$

TiO_2:

$$Ti^{4+} + H_2O_2 \xrightarrow{H^+} H_2TiO_3 \cdot H_2O_2 \qquad (14)$$

Al_2O_3:

$$Al(OH)_3 + 6F^- + Na^+ + 2K^+ + 3HCO_3^- \longrightarrow$$

$$\longrightarrow 3CO_3^{2-} + 3H_2O + K_2NaAlF_6 \downarrow \qquad (15)$$

Thermometric methods can be used if the "sensitivity" of reaction, that is the thermal effect arising during the measurement, is sufficiently high. This condition is fulfilled for the above reactions with the bauxite analysis.
It can be stated in general, that the thermometry is advantageous for the determination of elements being present in high concentration, thus for bauxite, too. (13)

Nuclear Analysis of Bauxite and Red Mud

The nuclear measuring technique, primarily the neutron activation analysis is widely used recently for the rapid quantitative analysis of the main components of bauxite and red mud. (32, 33)

The method is based on the phenomenon according to which part of the atomic nuclei in the sample exposed to the radiation of neutrons are converted to radioactive atomic nuclei. After the activation the resulting radioactivity can be detected by the measurement of the radiation.

The rate of activation of the elements present in the sample depends on the properties of the atomic nuclei of the same, moreover the intensity and duration of the irradiation and the concentration of the element in the sample.

With usual bauxites and red muds on applying a short time irradiation by slow neutrons mainly the aluminium gets activated, by fast neutrons in turn the silica and sodium.

Under those circumstances the activation procedure produces short half-life radioisotopes the activity of which cease within a few minutes thus the samples are practically inactive after the measurement and do not require any protection against radiation. Main advantage of the method lies in the fact that in contrast to the wet chemical analyses little sample preparatory work is required. Due to the high penetration power of the neutron radiation uniform irradiation is performed over the total volume of the sample the only measure to be taken is to fill up uniformly the tube with the sample material ground to 1 mm grain size. The resulting radio-isotopes also possess high penetrative beta and gamma radiation. The measurement of the same is carried out automatically without getting into contact with the material. Thus after having the sample filled into the tubes no further manual work is required. With Hungarian bauxite mines and alumina plants the natively developed make of an "Automatic Bauxite Analyzer" ("BEA") is used extensively. Its sample storing capacity is for accomodating 10 pairs of sample tubes simultaneously. A pneumatic tube dispatch system serves for the passing of tubes to the activation and measuring position and for the changing over of the samples. Any number of runs or repeated measurement of the samples can be carried out. The nuclear reactions having maximum yield taking place in the course of activation in the case of bauxites and red muds, are as follows:

^{27}Al (n,gamma) ^{28}Al
^{28}Si (n,p) ^{28}Al
^{23}Na (n,p) ^{23}Ne
^{23}Na (n,alpha) ^{20}F

The measuring accuracy is disturbed if the sample comprises other elements easy to get activated. The most important interfering nuclear reactions are as follows:

^{31}P (n,alpha) ^{28}Al
^{51}V (n,gamma) ^{52}V

If the samples contain phosphorus and vanadium merely in hardly changing quantities their interfering effect can be eliminated by the calibration procedure.
The built-in processor of the "BEA"-unit prints the result of measurement converted into oxide values. The equipment has to be calibrated by means of samples containing known amounts of Al_2O_3, SiO_2 and Na_2O. The tubes should be filled with 10 g of sample each. One run of 10 pairs of samples takes about 1 hour. The use of the version of the X-ray fluorescent analysis applying nuclear radiation source is also spreading. For the determination of Ca, Ti and Fe content of the bauxites suitably selected radioactive radiating sources (^{55}Fe and ^{238}Pu) emitting soft gamma radiation are used. X-ray fluorescence is excited by means of these and low-selectivity radiation meter is used. The measuring accuracy is less than that of the energy-selective measuring systems, however, the unit is simple, and provides a cheap fast analytical method.

COMPARISION OF THE VARIOUS ANALYTICAL METHODS

We have to introduce some basic concepts in connection with error computation if we wish to make a comparison between the various analytical methods, for detailed account we refer to the special literature (34).

The accuracy (E_i) of a measurement is characterized by the difference between the measured (m_i) and the real value (x)

$$E_i = m_i - x \qquad (16)$$

The real value is not a known quantity, still it can be well approached if we compound a "reference sample" of pure materials, and the analysis is carried out on this sample with the given method.

The precision of the measurement is characterized by the difference in wich the single results differ from each other if the measurement is repeated several times. The deviation (D) shows the declination of the single measured value from the arithmetical mean (M)

$$D_i = m_i - M \qquad (17)$$

The standard deviation (δ) is used for characterizing this grade of declination

$$\delta = \pm \sqrt{\frac{\varepsilon \, D_i^2}{n}} \qquad (18)$$

where n = number of measurement
We shall use the standard deviation for characterizing the deviation in the followings.
It should be noted here that the standard deviation provides an approximative value; if the number of measurements is low other statistical computation methods are used (35).

We should like to draw the attention to the fact that the reproducibility of the measured values does not give any information about the accuracy of the method it means rather that the measured values are close to a value wich may significantly differ from the real one.

A measuring method can be considered optimum one if its deviation and accuracy are equal but this occurs rarely in the pratice.

Less precise methods (with great deviation) are not suitable to achieve better results even if we increase the number of measurements only a more punctual determination of the deviation is possible.

It is expedient to take the deviation of analitical methods into consideration in the technological calculations or otherwise we can get to incorrect conclusions.

Relatively little attention is paid to the accuracy and precision of the various analytical methods of certain components the effectiveness of the methods is overrated.

The special line of the laboratory making the analysis also effects the results the measurements of industrial laboratories (mines, factories) are more reliable.

We give two examples to illustrate the attainable accuracy and reproductibility. One is based on the data taken from the literature (36), the other on our own measurements.

The data taken from the literature involve analytical results measured by different laboratories. We have taken out the results achived by chemical methods AAS and X-ray spectrometry for comparison.

The components tested: SiO_2, Al_2O_3, Fe_2O_3 TiO_2 and CaO. Tests were carried out with a standard bauxite sample. Results are summarized in Table 3.3.

The results of our own investigations are calculated utilizing the measurement data of 4 laboratories. Tests were carried out on two bauxite samples each laboratory has performed parallel measurements and we had used the arithmetic mean of the results in our calculations.

Two gravimetric methods were used to determine SiO_2 two complexometric and a potentiometric measurement for Al_2O_3, chromatometric method for Fe_2O_3 and spectrophotometric method for the determination of TiO_2 were used. Results are summarized in Table 3.4.

It turns out clearly from the data of the two tables what deviations and accuracies can be expected when analysing the main components of the bauxite.
If results of different laboratories are compared the permissible deviation and the tolerance are recorded.

A lower tolerance can be chosen rather in case of identical analytical methods than in the case of different ones.

It is expedient to employ precise methods for technological investigations because smaller differences can be indicated with their help still we have to know the methods of the plant utilizing the results of the technological test to be able to compare the results.

Comparison of the Analytical Methods (Data from the Literature)

Table 3.3

Component	The number of measurements	Measured value %	Variation abs %	Accuracy deviation from the standard
	Chemical methods			
SiO_2	21	7,46	0,51	+ 0,10
Al_2O_3	20	54,24	1,13	+ 0,04
Fe_2O_3	20	23,51	0,86	+ 0,24
TiO_2	18	2,40	0,25	0,00
CaO	17	0,30	0,18	+ 0,13
	AAS			
SiO_2	3	7,78	0,54	+ 0,42
Al_2O_3	3	54,07	0,67	- 0,17
Fe_2O_3	3	23,06	0,47	- 0,21
TiO_2	1		-	
CaO	4	0,17	0,08	0,00
	X-ray spectrometry			
SiO_2	4	7,39	0,48	+ 0,03
Al_2O_3	5	54,93	1,89	+ 0,63
Fe_2O_3	5	22,89	1,39	- 0,38
TiO_2	5	2,58	0,25	+ 0,18
CaO	5	0,22	0,06	+ 0,05

Comparison of the Analytical Methods (Our Own Measurement)

Table 3.4

Component	Sample	The number of measurements	Measured value %	Variation abs %	Accuracy deviation from the standard	Method
SiO_2	1 A	10	4,05	0,07	+ 0,02	H_2SO_4
	1 F	10	6,31	0,11	- 0,02	
	1 A	9	4,07	0,10	+ 0,04	triacid
	1 F	8	6,32	0,08	- 0,01	
Al_2O_3	1 A	9	55,11	0,48	- 0,22	EDTA after separation
	1 F	9	51,08	0,53	- 0,31	
	1 A	8	54,99	0,77	- 0,34	EDTA after decomposing the complex
	1 F	8	51,11	0,65	- 0,28	
	1 A	4	54,87	0,80	- 0,46	Potentiometric
	1 F	4	51,27	0,85	- 0,12	
Fe_2O_3	1 A	9	23,40	0,18	0,00	Chromatometric
	1 F	9	18,81	0,23	- 0,16	
TiO_2	1 A	8	2,32	0,08	- 0,01	H_2O_2 - H_2SO_4 spectrophotometric
	1 F	8	2,46	0,16	- 0,03	
	1 A	7	2,35	0,16	+ 0,02	H_2O_2 - H_2SO_4 - H_3PO_4 spectrophotometric
	1 F	7	2,48	0,25	- 0,01	

8. DETERMINATION OF MAJOR IMPURITIES OF BAUXITES

Bauxite as a sedimentary rock comprises also several impurities besides its main components (Al_2O_3, Fe_2O_3, SiO_2, TiO_2 and H_2O). Some of those elements influence the technological process (e.g. organic carbon, carbonate, sulfide, etc.) and some of them in turn, get enriched in the process circuit and contaminate the final product alumina (e.g. V_2O_5, P_2O_5, etc.). Some impurities can be recovered from the Bayer-cycle as valuable by-products (e.g. vanadium salt). Major impurities of bauxite are enumerated in the order of importance in Table I. The impurities are commonly figuring in the range 0.01 to 1 %, however, in some extreme cases (primarily in the samples of the bauxite prospecting work) they go fairly beyond 1 %.

The impurities are commonly expressed in terms of oxides. Total sulfur content is calculated in terms of SO_3 and within this value sulfide and sulfate content is also established. Other anions are expressed as anions (e.g. fluoride, chloride, etc.). This is particularly useful in the calculation of the diffraction mineral composition. The Fe(II) is used to be calculated as FeO.

As it had been already mentioned under Chapter 5 for the determination of those major impurities usually special methods are used. From the aspect of wet analysis the following should be kept in view:

- separation from the interfering main components
- separation from the interfering major impurities and trace elements
- adoption of specific reactions and methods if possible where the interfering effect of those impurities can be neglected.

That is why the separation by distillation (organic carbon, CO_3^{--}, F^-, etc.) or the AAS methods are often used.

For the determination of part of the elements enumerated in the table I. (Ca, Mg, Mn, V, Cr, Zr) the emission spectrum analysis is highly suitable.

EMISSION SPECTRAL ANALYSIS

Spectral analysis of the additional components of bauxite can usually be carried out directly from the pulverized sample. Homogenized bauxite sample pulverized to below 0.09 mm and dried at 110 °C is homogenized in the agate mortar with pulverized cobalt and pulverized graphite powder at a ratio of 5:1:10. The homogeneous mixture is placed into the carbon cup electrode. The upper electrode is a rounded-off-end graphite electrode. The exposures are made under a direct current arc at current intensity of 10 A. The sample to be tested is used as the anode. The method of complete burn-off is used in order to avoid components easy to volatilize from partial distilling away. Cobalt powder is used as a so-called inner standard. For the evaluation it is expedient to adopt the following analyzing line pairs:

Analysing Line Pairs

Table 3.5

Component	Line pairs used, Å	Concentration (lower limit) %
CaO	Ca 3179.3/ Co 3072.3	0.1
	3158.9/ Co 3072.3	
MgO	Mg 2790.8/ Co 2632.2	0.05
MnO	Mn 2933.1/ Co 2632.2	0.1
V_2O_5	V 3102.3/ Co 2632.2	0.05
Cr_2O_3	Cr 3015.0/ Co 2989.6	0.01
ZrO_2	Zr 3273.0/ Co 2989.6	0.01

The evaluation takes place by means of reference samples. At the spectral analysis of the major impurities a relative error of 20 to 25 % should generally be reckoned with.

DETERMINATION OF THE IMPURITIES

Determination of Calcium Oxide

Calcium is mainly represented in bauxite in the form of the following minerals: calcite $CaCO_3$, dolomite $CaMg(CO_3)_2$, gypsum $CaSO_4.H_2O$ and apatite $Ca_5(F,Cl,OH)(PO_4)_3$. (37) Its determination may be performed, as it was done earlier, by the classical gravimetric method after the separation from the main components, namely silicon, aluminium and iron (19) or by the volumetric EDTA method.

Today the AAS can be considered to be a good and fast method for the determination of little quantities of CaO in bauxite. The measurement can equally be performed from the stock solution made after the separation of SiO_2 or from the solution of the fusion made by $SrCO_3 + H_3BO_3$ for the determination of main components of bauxite the test being carried out in the N_2O/acetylene flame. The variation coefficient of the determinations of calcium by AAS is 5 %.

Ca-content of bauxites is fairly determinable by the X-ray spectrometry. If CaO-content exceeds 0.5 % the bead fusion method described under Chapter 7 can be used. In case of less CaO-content than 0.5 % and owing to the dilution occurring at the bead preparation it is more advantageous to carry out the test on tablets pressed of 30 μm size pulverized material without dilution and any bonding material. In case pressed tablets are used the determination accuracy for calcium is 2 to 3 rel %. Its time requirement is about 15 minutes.

Determination of Magnesium Oxide

Some 0.1 % of magnesium oxide present in the bauxite is mainly represented in the form of dolomite. The enrichment in dolomite can be detected in the Halimba (Hungary) bauxites (37).

The magnesium content has been formerly determined by the wet chemical method, gravimetrically as $Mg_2P_2O_7$. Recently the EDTA determination is used (24). These determinations are lengthy because they require much precedential separation procedures. The scheme of the classical separation is given in Fig. 3.9. The complicated separation procedures indicated in the figure can be by-passed if the determination is made by the AAS method. This can be carried out from the stock solution made of the filtrate of the SiO_2 - without further separation - or from the direct fusion described for the main components of bauxite (Part 7.). The AAS measurement is carried out in the acetylene/air flame. Relative error of the method is 5 %. Evaluation is made by a calibration curve. Further advantage of the AAS method is that little MgO-contents (0.01 % magnitude) can also be determined.

Determination of the Oxides of Manganese

Manganese occurs in bauxites in the magnitude of order ranging 0.01 to some 0.1 %. No uniform calculation of manganese content exists. MnO, Mn_3O_4 is commonly established, expressing as elementary Mn would be correct. Most frequent minerals are hausmannite ($Mn_2.MnO_4$) and lithiophorite ($Li_2Al_8Mn_2^{++}Mn_{10}^{+4}O_{35}.14H_2O$). In some bauxites the occurrence of Mn exceeds 0.5 % (e.g. the Jamaican bauxite). Manganese content can be determined spectrophotometrically from the stock solution resulting after the separation of SiO_2. Manganese is oxidized with potassium periodate in sulfuric acid medium to permanganate (MnO_4^{--}) the violet colour of which is measured spectrophotometrically. The method is very accurate with a relative error less than 5 %. By the use of the differential spectrophotometry the error can be further reduced.

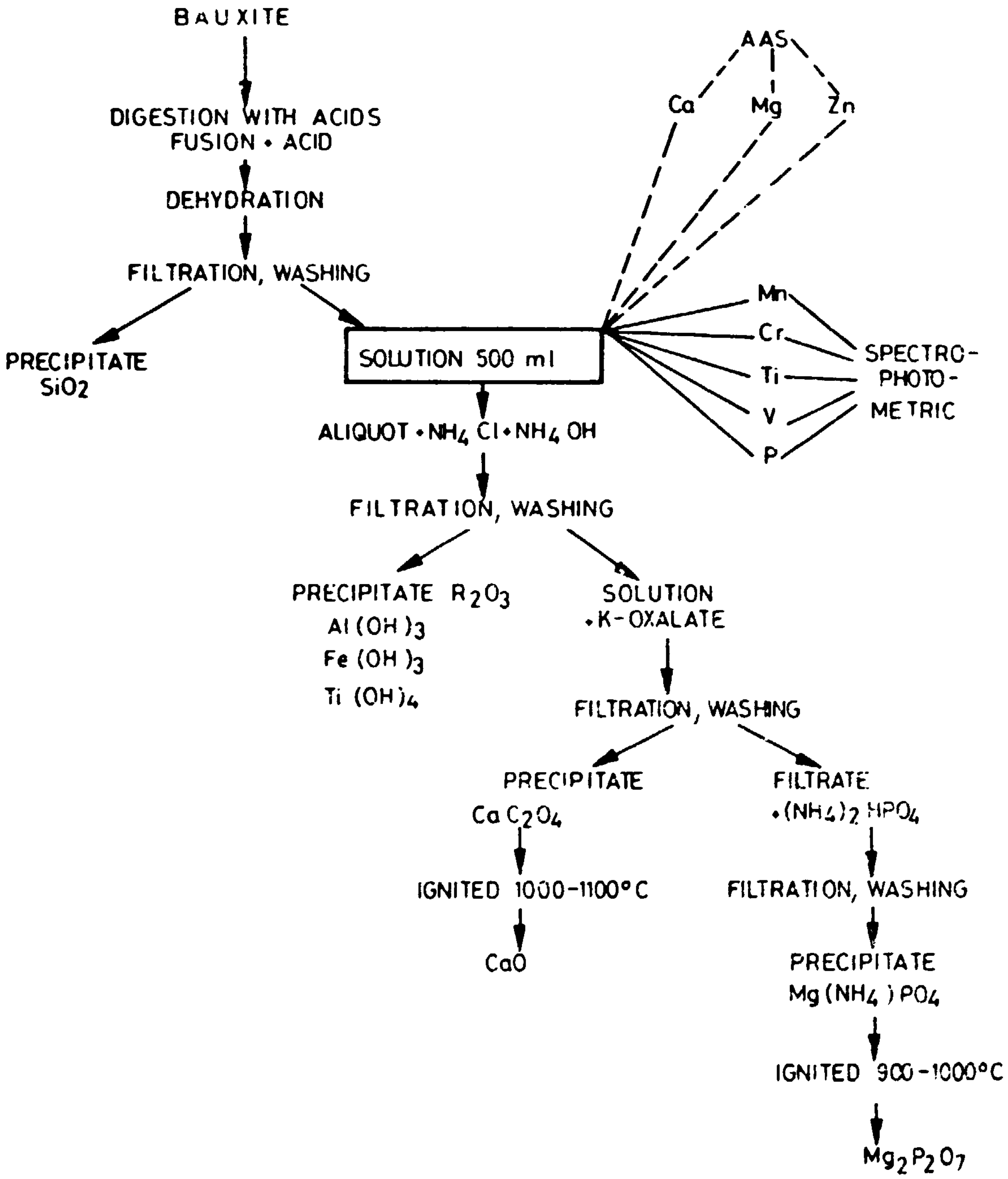


Fig. 3.9

WET CHEMICAL ANALYSIS OF THE BAUXITE

Determination of V_2O_5 and Cr_2O_3

V_2O_5 and Cr_2O_3 occurs in bauxite in 0.01 respectively 0.1 order of magnitude, mainly as an accompanying substance of the iron minerals (embedded) and in the form of vanadate. Chromite mineral (Cr_2FeO_4) has been identified in Hungarian bauxites (37).

The vanadium can be recovered as a valuable by-product of the Bayer-type alumina production. During the digestion about 30 % of the V_2O_5-content of the bauxite gets enriched in the aluminate liquor in the form of Na_3VO_4 and forms crystalline salts with the phosphate and fluoride present in the aluminate liquor ($2Na_3VO_4.NaF.19H_2O$) (38), respectively $2Na_3PO_4.NaF.19H_2O$ (39). The crystalline salt can be removed by cooling from the process circuit. This so called vanadium salt is a valuable raw material for the purpose of producing sodium polyvanadate or V_2O_5. Thus the examination of the V_2O_5-content of bauxites is of primary importance.

During the wet chemical determinations, as mentioned already the separation procedure from the main components is indispensable. Since iron is a component easy to oxidise or reduce, as well as colourful component in acid medium (highly interfering with photometric methods) primarily the large quantities of iron should be separated. The oxidising fusion with NaOH is very suitable for this purpose during which many of the accompanying elements and trace contaminants dissolve quantitatively (see Fig. 3.10.

At the alkaline oxidising fusion all the elements irrespective of any mineral form become digested i.e. the absorption effect of the iron precipitate has to be reckoned with. This can be avoided by making stock solution then filtering an aliquot portion and carrying out the examination within a short time. The determination of V_2O_5 and Cr_2O_3 can be carried out from the solution by titrating the V(V) and Cr(VI) by

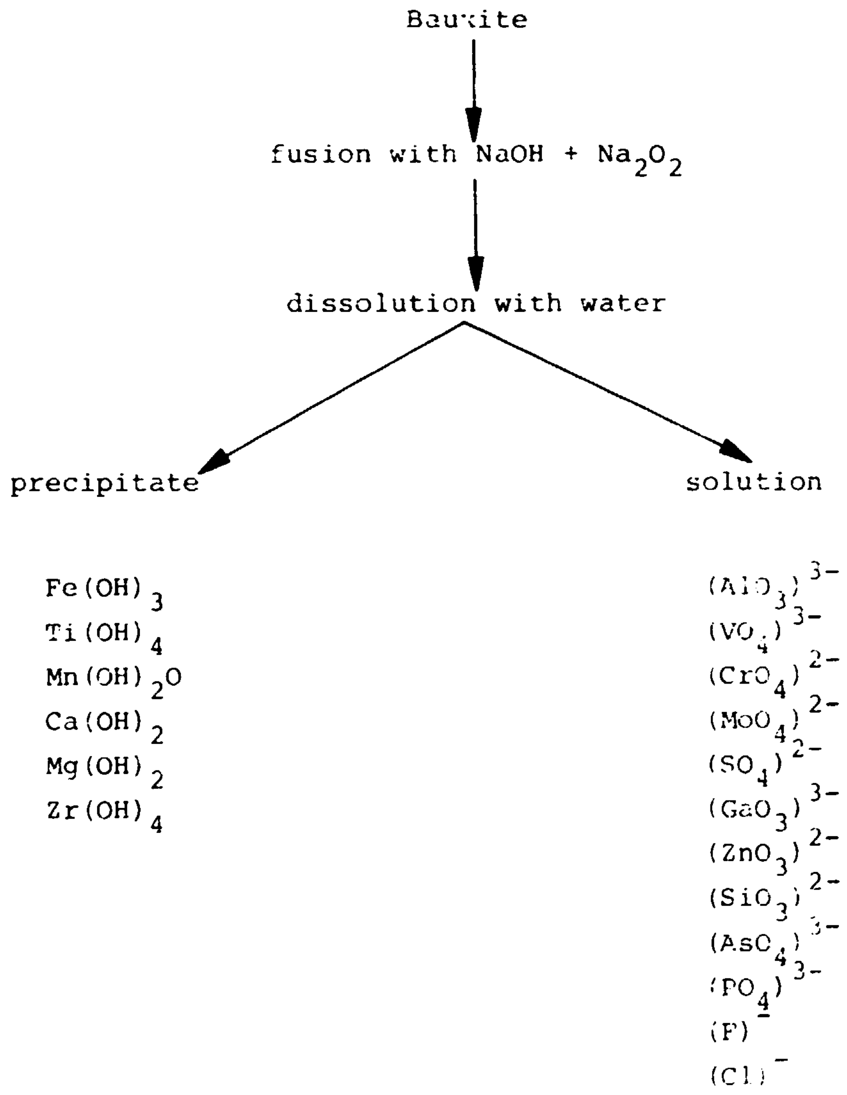


Fig.3.10

SEPARATION OF THE MAJOR IMPURITIES AND TRACE ELEMENTS OF THE BAUXITE means of Fe(II)-ammonium sulfate standard solution (Fe(II).$(NH_4)_2(SO_4)_2.6H_2O$) up to the potentiometric end point indication (platinum - calomel electrode). Then it should be oxidised cold by $KMnO_4$, in this case vanadium oxidises to V(V) only and after decomposing surplus permanganate it can be measured by Fe(II) standard solution. When subtracting the standard solution consumed for V_2O_5 during the second titration from the summary of the first titration V_2O_5 + Cr_2O_3 the consumption of iron (II) standard solution equivalent to Cr_2O_3 is obtained. For the analysis it is expedient to start with 5 g material. Because of the high accuracy (3 to 5 rel.%) of the method it is expedient to adopt it for research work or dissolution balances.

V_2O_5 may also be determined from bauxite by means of the photometric method. After the alkaline oxidising fusion the vanadium (V) forms a colourful complex compound with sodium-phosphorus-tungstate or N-benzoyl-N-phenyl-hydroxyl-amine. The complex compound can be extracted from the acid medium by chloroform.

For the determination of Cr_2O_3 the highly sensitive biphenyl carbazide photometric method is commonly used.

Determination of P_2O_5-Content

P_2O_5-content of bauxites varies within wide limits ranging some 0.01 % to 1 %. Most important phosphate minerals of carstic bauxites are crandallite $CaAl_3H(OH)_6(PO_4)_2$, apatite $Ca_5(F,Cl,OH)\ (PO_4)_3$. Furthermore fermorite ($CaSr(F)PO_4$) and monazite $CePO_4$ also contain phosphorus.

Major part of the phosphorus gets in form of Na_3PO_4 in the alkaline phase during digestion and becomes enriched there. Part of it is removed by the vanadium salt.
If the digestion of bauxite is performed in the presence of

lime the amount of phosphorus getting into the aluminate liquor is by far less, because it forms $Ca_3(PO_4)_2$ and gets into the red mud. The analytical chemical determination of the P_2O_5-content can be performed by the classical gravimetric method as $(NH_4)_3P(Mo_3O_{10})_4$ or after having it dissolved by alkaline solution the same can be determined titrimetrically by back-titrating the alkaline solution. Recently exclusively spectrophotometric methods are used. The determination takes place from the stock solution made of the filtrate of SiO_2 and colour intensity of the blue phosphorus-molybdate complex is measured. The error or the method is 10 rel.% for cases below 0.1 % and 5 % for cases above this figure.

No other instrumental methods (X-ray spectrometry) are used for the determination of P_2O_5-content.

Determination of Fluoride Content

Some bauxites contain fluoride at a concentration ranging 0.01 to 0.1 %. Fluoride is likely to be mainly represented in the mineral form of apatite $Ca_5(F,Cl,OH)(PO_4)_3$. When digesting bauxite major part (70 to 80 %) of it gets into the liquor in the form of NaF and gets enriched there. Minor portion of it is removed from the system along with the vanadium salt, $2Na_3VO_4.NaF.19H_2O$. Causticization also reduces it considerably.

Aluminium interferes with the determination of fluoride should it either be made volumetrically or spectrophotometrically, so it has to be separated. The Willard-Winter distillation method is best for the separation (40), according to which H_2SiF_6 is distilled from the sulfuric acid medium by steam stripping. Fluoride concentration can be measured in the distillate either titrimetrically by $Th(NO_3)_4$ standard solution or spectrophotometrically by alizarine or as it is recently done by the use of fluoride-selective electrodes (41) (see Part 5.).

Fluoride content of the bauxite can generally be determined with a relative error of 5 %. The organic substance in bauxite does not interfere with the volumetric determination.

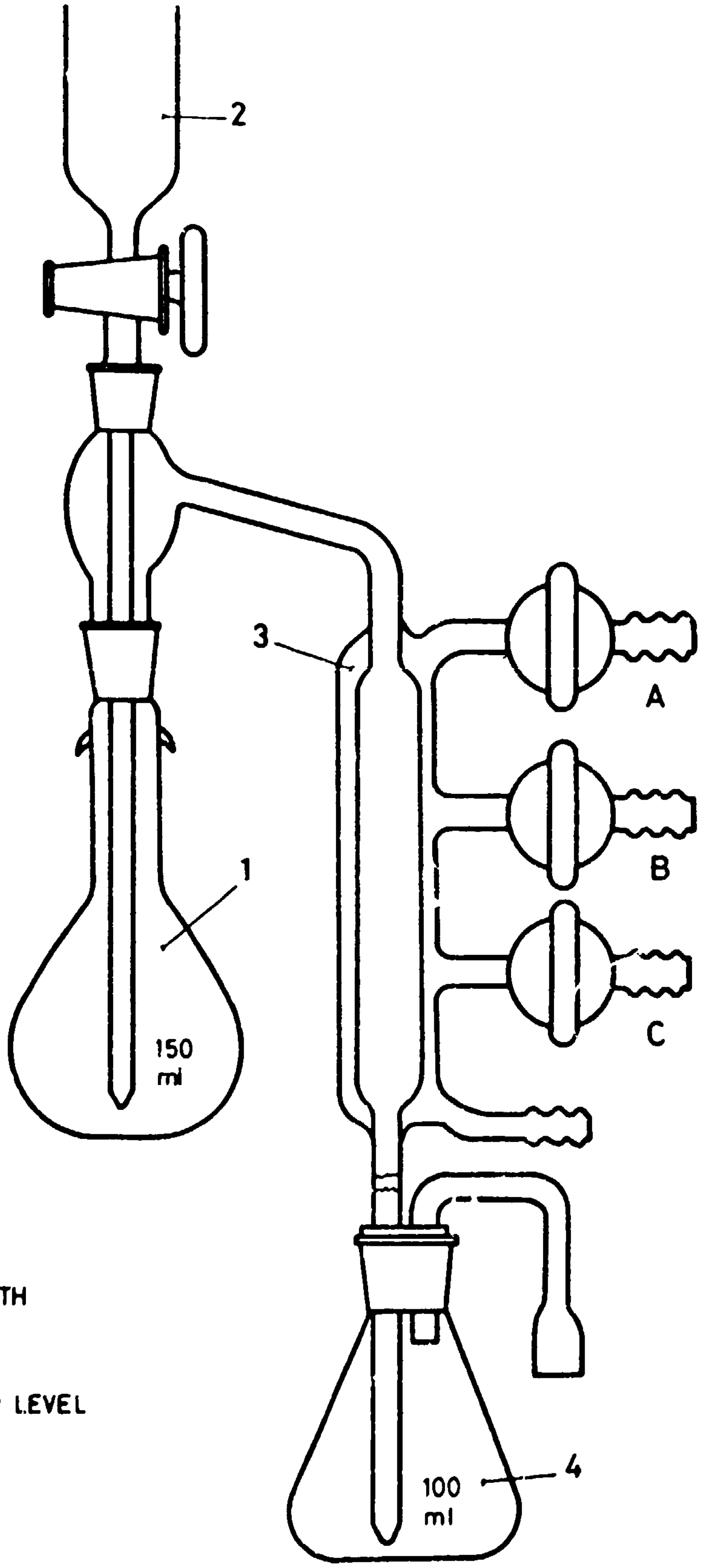
Carbonate and organic impurities occurring in bauxites play an important role in the Bayer technology.

Both impurities get considerably enriched in the process circuit and cause technological problems if they exceed certain concentration values. Owing to those mentioned above it is important to determine their percentage in the bauxite and though their quantity is comparatively little yet they are counted as important components.

Determination of the Carbonate Content

The carbonate minerals easily decompose under the effect of acids while releasing CO_2. The decomposition is actually rapid in the case of carbonate minerals, in carbonate-holding rocks if the carbonate mineral is located in the internal part of the particle or it is covered with another crust hard to dissolve the velocity of dissolution gets considerably moderated. The entire amount of CO_2 can generally be released by the complete dissolution of the sample and separated by a longer distillation.

For the determination of a smaller amount (up to few %) of CO_2 the distillation method is recommended (42). 30 to 40 % phosphoric acid solution is suitable for the decomposition of carbonates. The incipient CO_2 along with the condensing vapour is received in a known amount of $Ba(OH)_2$ solution. The apparatus for the determination of CO_2 is shown in Fig. 3.11. The procedure requires much care and the attention to some sources of error is drawn here below:



1. FLASK
2. DROPPING FUNNEL
3. COOLER
4. RECEIVING BEAKER WITH $Ba(OH)_2$ SOLUTION

A, B, C · COOLING WATER LEVEL CONTROL

Fig. 3.11
CO_2 DISTILLATION APPARATUS

CO_2 loss may occur during the deaeration of the distiller because of the hydrolysis of the carbonates. The error can be eliminated by the addition of a small amount of $Ba(OH)_2$.

The presence of much Mn(IV) compound can cause positive error because part of the organic impurity could oxidise to carbon dioxide. The error is not significant and by the addition of some reducing agent e.g. hydroxylamine sulfate it can be eliminated.

Any volatile acidic component causes positive error, when carrying out very exact investigation, this also has to be reckoned with.

In addition it should be noted that the carbonate content of red muds can also be measured by means of the above method.

For the determination of a larger amount of carbonate it is more expedient to adopt the gravimetric method (19), by the use of phosphoric acid already described for the dissolution of the sample.

Determination of the Organic Substance

After having eliminated all the carbonate content of the sample the oxidation made in the liquid phase can be used for the determination. A precondition of the accurate measurement is that the CO_2 resulting from carbonates is driven off but at the same time the loss of volatile organic compounds is avoided. During the removal of carbonates, if the sample comprises oxidising material (e.g. MnO_2), the oxidation to CO_2 of the organic substance should be inhibited. In the course of preparation the organic inclusions should also be released. Finally the organic material content of the sample should be fully oxidised to CO_2 in the liquid phase.

Phosphoric acid is suitable for the decomposition of carbonates. When carrying out the decomposition with the reflux condenser even after two hours boiling no losses in organic substance can be observed and the CO_2 completely escapes. Adequate concentration phosphoric acid can even release organic substances from the inclusions. If it is inferred that the organic substance gets oxidised the addition of a reducing agent would eliminate the error. Formerly chromic acid or dichromate had been used as an oxidising agent. The oxidation by chromic acid is not complete (43), the more drastic potassium peroxydisulfate ($K_2S_2O_8$) can be used instead but only if the oxidation is catalyzed by silver ions (Ag_2SO_4).

Of course, the chemicals used should contain organic contaminations only in traces. This relates also to the measuring device, notably tap grease must not be used for grindings and traps.

Particular care should be taken to avoid any organic contamination when the maipulation is made. If the material to be tested takes its origin from a drill hole sample one should gather information about the condition whether for the flusing of the bore hole any liquor containing organic substance has been used or not. If so, the sample is not representative from the aspect of determination of organic substance.

Similar error occurs if the sample is sieved through a sieve the cloth of which being made of some kind or organic fibre. The vapours of the softening agent of the plastic bags used for packing may also cause problems.

The oxidation is carried out in the apparatus shown in Fig.3.12. The role of its sections is the following:

1. Reaction vessel, serving for the oxidation taking place there, heated by controllable electric range
2. Dropping funnel for the oxidising agent.

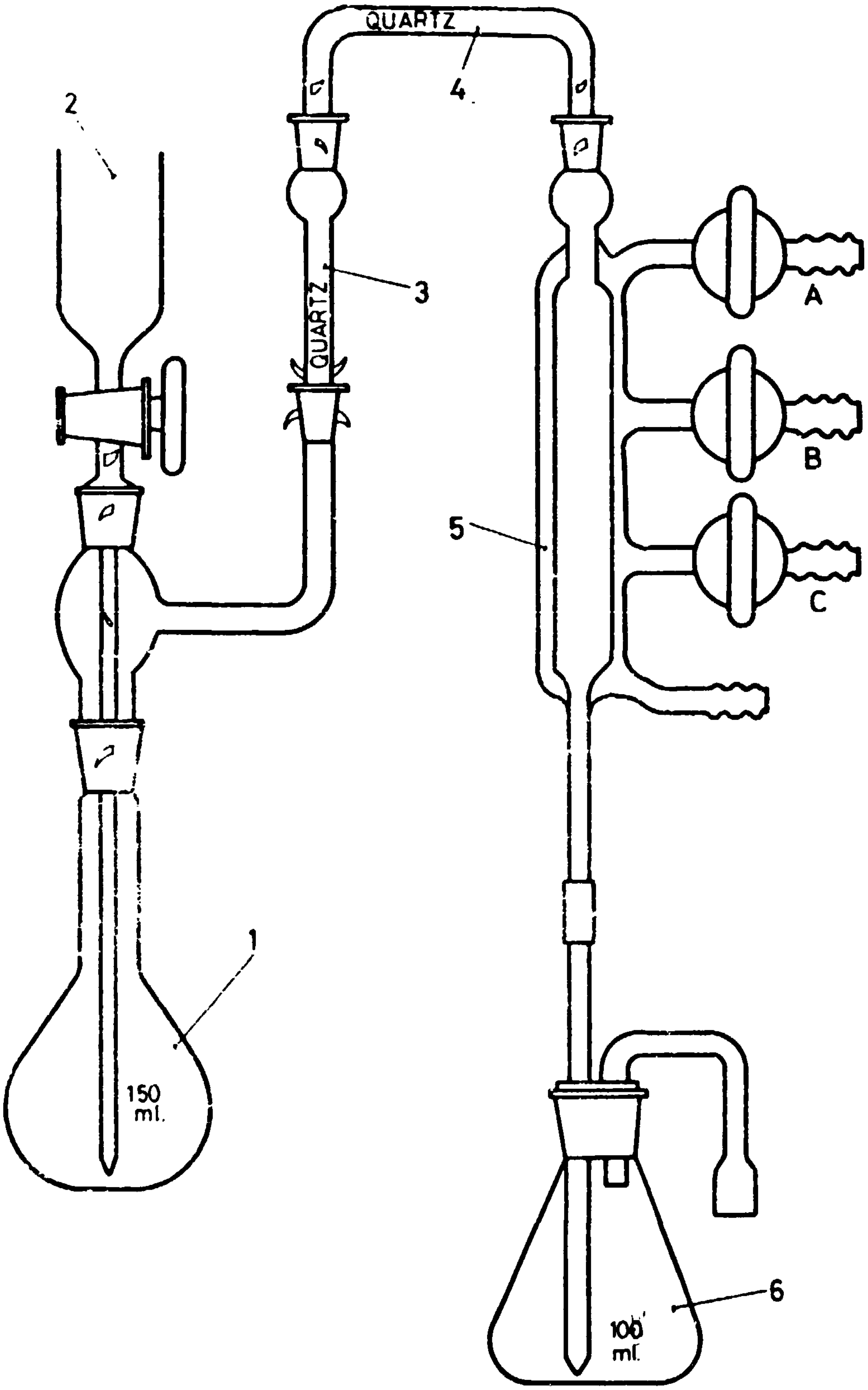


Fig. 3.12

DISTILLATION APPARATUS FOR THE DETERMINATION OF ORGANIC - MATERIAL

3. Electrically heated quartz tube with manganite filling for the purpose of the oxidation of the volatile organic substances.
4. Electrically heated quartz tube with copper metal filling. The latter binds the oxygen gas evolved from the oxidising agent. The CuO formed at the same time additionally oxidises organic compounds possibly not having been oxidised in the tube 3. (The absorption of the oxygen gas is the precondition of proper running of the cooler No.5.)
5. Cooler-condenser.
6. Receiving flask.

A,B,C, valves for cooling water level control.
Operation of the apparatus is outlined in the practical section.

Determination of the Sulfur Content

Sulfur is generally represented in the bauxite in the form of sulfide and sulfate at a rate of 0.01-0.2 %. In some grey pyritic bauxites the sulfur content may be even much higher.

Sulfide mineral of the carstic bauxites is pyrite FeS_2 and marcasite FeS_2 its accompanying mineral. The amount of the latter is far less than that of the pyrite. In addition minor quantities of sulfide may occur in the form of sphalerite, ZnS and galenite, PbS. The group of sulfate minerals is large so here only the most important ones will be enumerated.: alunite $(NaK)Al(OH)_6(SO_4)_2$, aluminite $Al_2(OH)_4(SO_4).7H_2O$, melanterite $FeSO_4.7H_2O$ and rozenite $FeSO_4.4H_2O$. In addition there are the alkali-earth sulfates e.g. gypsum $CaSO_4.2H_2O$, anhydrite $CaSO_4$, barite BaSO, celestite $SrSO_4$, etc.

The crystalline pyrite does not alter during digestion and gets entirely into the red mud. Less stable sulfide minerals are attacked by caustic and finally after oxidation they will figure as Na_2SO_4 in the liquors. If bauxite is abundant in sulfide minerals the red mud assumes inferior character as far as settling is concerned.

This is the reason why the total sulfur moreover the sulfide sulfur and sulfate sulfur content of bauxites has to be determined accurately.

Total sulfur content can be accurately and properly determined either after the alkaline oxidising fusion or after the oxidising digestion made with Lunge acid (inverse aqua regia) by the gravimetric method, the resulting $BaSO_4$ precipitate weighed or by the combustion method during which the total sulfur content is burnt to form SO_2, the latter being measurable by the iodometry according to the following equations:

$$SO_2 + H_2O = H_2SO_3 \qquad (19)$$

$$H_2SO_3 + J_2 + H_2O = H_2SO_4 + 2HJ \qquad (20)$$

Recently the automatic target instruments enable the direct IR detection of SO_2 releasing during combustion. (For example: LECO CS-46 type).

Sulfide sulfur. It is a pity that no reliable analytical method for the determination of sulfide sulfur from bauxite is at our disposal. Thus the sulfide content can only be measured indirectly:

$$S_{sulfide} = S_{total} - S_{sulfate}.$$

Sulfate sulfur is determined gravimetrically after the alkaline fusion. This method yields good results only for low (less than 0.5 %) SO_3-content. In case of high pyrite bauxites the method is unreliable.

As the sulfur content of the normal industrial bauxites is generally low, i.e. 0.1 to 0.2 % (in terms of SO_3) the determination of the total sulfur content is generally sufficient (and this is usually expressed in terms of SO_3).

Determination of Iron (II) content

Minerals containing bivalent iron also occur in bauxite (i.e. siderite $FeCO_3$, etc.) and sometimes the knowledge about them is essential. The hydrofluoric-sulfuric acidic dissolution as used for silicates (26) is adopted for their determination. The procedure should be conducted by the exclusion of air or in an inert gas atmosphere /in order to avoid the oxidation of Fe(II)/. Boric acid is added in order to bind hydrofluoric acid and iron (II) is measured oxidimetrically by $K_2Cr_2O_7$.

Fairly reproducible results can be expected with this method in case the investigation specifications (grain size distribution, measured out charge, amount of acid, heating time, inert gas atmophere, etc.) are precisely observed, despite the error of method exceeds 10-25 %.

The thermometric method can favourably be used for the determination of siderite ($FeCO_3$) content of bauxites.

The essence of the method is that the Fe (II)-content is partially dissolved in the presence of excessive, however, known amount of oxidising agent ($K_2Cr_2O_7$). At a suitably chosen acid concentration the carbonate easy to dissolve dissolves and the incidental magnetite (Fe_3O_4) remains practically unchanged. Likewise the compact form of pyrite interferes a little, in the presence of finely distributed pyrite positive error should be reckoned with.

An excess of oxidising agent during dissolution excludes the interfering effect of the oxygen content of the air and back-titration with a reducing reagent ($FeSO_4$) can be performed without the need of filtering the undissolved residue of the sample. The method is applicable for siderite content exceeding 1 %.

Determination of ZrO_2-Content

Bauxites generally comprise some hundredths % of ZrO_2. This can usually be found in the form of ZrO_2. It does not dissolve in caustic during digestion, thus it gets entirely into the red mud.

Zircon is mainly determined by spectral analysis in accordance wit those described on page 3-o4. Its determination may also be solved by the spectrophotometry (by alizarine, Asenazo III, xylenol-orange), however, it is rarely used due to its circumstantial character, (and because of the indifferent behaviour of ZrO_2 in the Bayer process circuit).

9. DETERMINATION OF THE TRACE ELEMENTS OF BAUXITES

The most important trace elements are indicated in Table 3.1. These trace elements occur in the magnitude of order ranging 0.1 to 100 ppm, yet some of them exceed also 100 ppm. In some bauxites, for instance, Na- and K-content can get enriched up to 0.1 %. The Zn-content of bauxite frequently attains at 200 to 400 ppm. Similarly Ce of the rare earths can exceed 100 ppm. The other trace elements are figuring within the range 1 to 60 ppm in general. Since the way of mineral bond of these trace elements is uncleared in most cases it is expedient to calculate and establish the same in the elementary form rather tnan in oxides. Some of the trace elements getting into the Bayer process circuit become enriched in the liquors to such an extent that even the recovery can be economic, as in the case of gallium. Mo becomes similarly enriched in the liquors.

Other part of the trace elements, however, is undesirable in the process circuit because they adhere to the hydrate and contaminate the final product alumina (i.e. by Zn, Cu, etc.) In the plants the spectral analysis is commonly used for the determination of trace elements of bauxite. The method described for the main impurities of bauxite (see p. 3-74) is commonly adopted by the use of Co internal standard. By this method Ga, Mo, Ni, Cu, Be, As-content of bauxite is commonly determined.

Apart from the spectral analysis mainly the wet chemical, primarily spectrophotometric, organic extraction combination spectrophotometric AAS and flame photometric (Na, K) methods are commonly used.

Determination of Gallium

Ga-content of bauxites comes to about 10 to 60 ppm (44). Two third of it gets into the process circuit. Its recovery from the Bayer process circuit is economic. Apart from the spectral analysis, Ga can be determined by making the complex compound formed with malachite-green, then extracting by benzene and measuring the colour intensity. In order to eliminate the interfering effect of the interfering Fe (III)-ions they are reduced by $TiCl_3$ to Fe (II). The determination can be made from the stock solution prepared from the filtrate of the SiO_2. Relative error of the measurement is about 10 %.

Determination of Molybdenum

Bauxites comprise also molybdenum in the range 5 to 30 ppm (44). One half of the amount of Mo charged with bauxite gets into the process circuit the other half leaves with red mud and alumina, respectively. The portion of Mo present in the process circuit does not adversely affect the quality of alumina because the oxide of molybdenum (MoO_3) is a volatile compound and alumina gets released from it during the calcination.

Apart from the spectrum analysis, Mo can be determined by precipitating it with α-benzoinoxime and using polarography after the separation of the former. There is also a possibility for the photometric determination (23).

Determination of Zinc Content

Bauxite usually comprises also zinc in the magnitude of 100 ppm. 30 % of it dissolves, the balance leaves with red mud. Most of the zinc getting into the liquid phase gets deposited on the hydrate particles during the precipitation process and finally contaminates the alumina. Zinc is an undesired contaminant at the electrolysis because it enters the aluminium metal.

For the determination of the Zn Content the AAS method is the best one. The determination may be carried out directly from the stock solution made of the filtrate of SiO_2 (see Fig.3.9). The measurement is conducted in the acetylene/air flame. The

relative error of the measurement is 2 %. In addition, there are some spectrophotometric methods referred to in the literature (23).
Zn-content may also be measured polarographically.

Determination of Ni, Cu, Be-Content

The determination of Ni, Cu, Be represented at level of 10 ppm or below takes place by the spectral analytical method, however, one may find also fairly elaborated spectrophotometric procedures in the literature. Those methods, however, requiring lengthy separation and concentration procedures are rarely adopted.
The trace elements in question generally do not interfere with the Bayer process and contaminate alumina only to a minimum extent. (Ni and Cu may figure to less than 10 ppm in the alumina. The Be may be of interest as Al indicator (see Vol.1.)

Determination of As

Some bauxites comprise also As in the magnitude of about 10 ppm. Almost the entire amount (~90 %) of the arsenic dissolves in the process liquor and can be removed from it along with the vanadium salt.

The best method for the determination of the arsenic is the one after the destruction of the organic substance of bauxite the distillation of $AsCl_3$ from the HCl medium. From the distillate arsenic can be measured by the end-point potentiometry using $KBrO_3$ standard solution. The bromate solution oxidises As(III) to As(V). It is advisable to start with a measured-out charge of 5 to 10 g.
Relative error of the measurement is about 5 %.

The As can also be oxidised in the distillate and determined by ammonium molybdate in the form of molybdenum-blue by means of the spectrophotometry. The error of this method is somewhat higher than that of the titration. Its advantage, however, is that weighing-out charges (0.5 to 1 g) are sufficient. The As-content can be measured by spectral analysis, too.

For the investigation of K, Na-content of bauxites the flame photometric respectively AAS methods are expedient to be adopted. The determination of these constituents is motivated mostly for research type work.

The occurrence and behaviour of RE in the Bayer process circuit is reported by Logomerac (45). At the determination the total RE is used to be measured spectrophotometrically. The individual determinations are made by the instrumental methods (MSP spectrum analysis, activation analysis, etc.).

It comes rarely to the determination of the rare elements figuring in Table 7, however, not being dealt with in detail. Their investigation is requested for the research work in general. For their determination mainly the spectrophotometric methods are used (23).

Detailed description about the trace elements occurring in bauxites is given by Pearson (46). Their behaviour in the Bayer process circuit is dealt with in detail by Logomerac (4[illegible]).

10. DETERMINATION OF THE MAIN CHEMICAL COMPONENTS OF RED MUD

The determination of main components of red mud is essentially identical with those described with bauxite. There is some deviation in as much as red mud contains the main components of bauxite in a ratio different to the latter and depending on the technology one or two main newer components also enter the system, i.e. Na_2O or Na_2O + CaO.

In addition same change of the methods outlined with bauxite may also be necessary due to the shift in proportions.

CHANGE OF THE ANALYTICAL METHOD DUE TO SHIFT IN PROPORTIONS OF THE MAIN COMPONENTS

Substantially three components may require a modified analytical procedure: the measurement of SiO_2, Al_2O_3 and TiO_2.

Variation of the method at the measurement of SiO_2

The gravimetric determination of SiO_2 can be misleading in the presence of alkali metals and alkali-earth metals for two reasons:

- in the presence of alkali metals dehydration of the silica gel is not completed, i.e. lack of SiO_2 arises,
- in the presence of alkali-earth metals a silica gel gets contaminated by alkali-earth metal sulfate, this is to be reckoned with during the further treatment of the precipitate.

The first fault can be avoided if the silica is separated by a double evaporation or if time is to be saved and minute amount of solved or colloidal SiO_2 is determined by a quick spectrophotometral method from the aliquot portion of the filtrate of the only once precipitated silica.

The $CaSO_4$ precipitating along with silica gel reacts with the SiO_2 at high ignition temperatures (1000-1100 ^{o}C) commonly used.

$$CaSO_4 + SiO_2 \longrightarrow CaSiO_2 + SO_3 \qquad (21)$$

After the fuming off with HF-H_2SO_4, $CaSO_4$ remains.

$$CaSiO_3 + H_2SO_4 + 4HF \longrightarrow CaSO_4 + SiF_4 + 3H_2O \qquad (22)$$

Thus the loss of weight presumed to be equivalent to the SiO_2 is doctored by the difference of molecular weight existing between $CaSiO_3$ and $CaSO_4$.

The error may be avoided if the ignition is carried out at 800 ^{o}C both for the silica residue and that of the fuming off procedure. With extreme SiO_2 to CaO ratios, for example causticized red muds, it is expedient to get leached CaO off by cooking with HNO_3, then the solution should be neutralized by NH_4OH, the R_2O_3 + SiO_2 precipitated and then SiO_2 can be determined after filtration.

Determination of Al_2O_3

Large amounts of CaO interfere with the determination of Al_2O_3. Therefore it is not expedient to use the separation by NaOH described above for the bauxite. Instead of this the processing of R_2O_3 precipitate separated by the hexamethylene tetramine method is recommended for the determination of Al_2O_3.

Determination of TiO_2

The spectrophotometric measurement of TiO_2 yields good results even in case of red muds. However, TiO_2 gets enriched to such an extent in red muds of high TiO_2 bauxites that the accuracy of the spectrophotometric determination is no more sufficient.
In this case the use of the differential spectrophotometry is advisable or the reduction by Hg-amalgam and the subsequent titration with Fe^{3+} standard solution. TiO_2, if being in greater concentration can also be measured by the thermometry.

Determination of Other Main Components

When measuring the adsorbed moisture, loss on ignition and Fe_2O_3-content the methods described with bauxite can be used without any modification.

Determination of the Two New Main Components

Determination of the Na_2O-content.

Na_2O-content of red mud originates from two sources:

- sodium aluminium silicates resulting during digestion, and
- the Na_2O-content of the adhering aluminate solution resulting from inproper washing of the red mud.

Thus between bound and soluble Na_2O-content are differenctiated. Commonly the summary of the two and the soluble Na_2O-content are determined.

Of the common methods serving for the determination of Na_2O the precision flame-photometric and the thermometric methods may be used. The flame-photometric method is the more advantageous one of these two methods.

Bound and soluble Na_2O-content of the red mud are equally soluble by cooking it with HNO_3-NH_4NO_3. The degree of leaching comes to 99.7 to 99.9 %. After the leaching the solution is alkalized by NH_4OH then the precipitate is filtered and washed. Then the Na_2O-content of the filtrate is determined by means of the flame-photometer or atomic absorption spectrophotometer in the emission. Precondition of a good measurement lies in the state of being capable of measuring with a relative error of 1 % by the instrument used. If greater measuring lots are used, the Na_2O-content can also be measured by the thermometry, however, this method requires some more time.

Arising from the feature of the task the measurement of soluble Na_2O produces only conventional results.

After aqueous cooking of the sample the alkalinity of the solution is titrated by standard acid solution or after leaching by ammonium hydroxide its Na^+-content is measured by the flame-photometer. The determination is an important task because it provides information about the NaOH-loss occurring during the processing technology.

Determination of the CaO-Content

The AAS method used with bauxite provides no more good results above 2 to 3 % of CaO-content.

Serviceable methods are: Precipitation of Ca-oxalate (CaC_2O_4) from a slightly acidified solution previously masked by EDTA-solution. Filtered and washed precipitate may be measured by the gravimetry or may be titrated by the standard $KMnO_4$ solution or determined by the acid-base titration.

From red muds containing large amounts (10 %) of CaO the amount of CaO can be measured by the thermometry by the use of $K_2C_2O_4$ reagent after having leached by nitric acid and alkalized by ammonium hydroxide.

Other Aspects for the Analysis of Red Muds

For the dissolution of red muds containing undigested diaspore the methods described for bauxites must be used.

If applying a low-temperature technology undigested quartz (SiO_2) remains in the red mud. Its quantity can be determined by the method outlined there.

The organic material content of red muds provides information about the level of the organic content in the process circuit. The principle of measurement is identical with that outlined under the analysis of bauxites.

11. DETERMINATION OF THE LESS IMPORTANT COMPONENTS OF RED MUD

The analytical determination of the less important components of red mud is essential from the following points of view:

- investigation of dissolution of the less important components and trace elements of the bauxite in the Bayer process
- determination of the total material balance of the less important and trace elements
- effect of certain less important elements on the sedimentation of red mud
- enrichment of the less important and trace elements in the red mud, their possible recovery for utilization purposes.

The most important tasks among them are the dissolution tests and the completion of total material balance. Knowing the quantities in the dissolution tests it is sufficient to determine the component required in bauxite and red mud.

As we have learned in the former chapter the main components of red mud have modified (compared with bauxite) Na_2O and CaO have become main components and the quantity of less important contaminating components and trace elements have changed similary. Their quantity increases in some cases (no dissolution takes place, or only to a negligable extent) or their quantity decraeses in some cases (dissolution).

It may be stated as a general case that the major impurities and trace elements of bauxite are tested with the analytical methods described already in connection with the bauxite.

Sometimes a modification of the analytical methods is required due to changes in the major components (Na_2O, CaO) and a significantly increased iron content.

A simple and quick method for the determination of the less important components of red mud is the emission spectral analysis mentioned in connection with the bauxite in chapter 8. The usage of reference standards corresponding with the composition of the red mud is essential during their emission spectral analysis (high Na_2O possibly high CaO). Bauxite reference standards are not adequate for this purpose. The usage of inadequate standards implies too great errors.

The altered composition of red mud has to be taken into consideration in case of AAS measurements as well, especially at the determination of MgO and ZnO.

12. CHEMICAL ANALYSIS OF SODIUM ALUMINATE LIQUORS

THEIR MAIN COMPONENTS AND IMPURITIES

Aluminate Liquor

Amphoteric elements can be made to dissolve both by H_3O^+ and OH^--ions hence they may behave as bases and as acids, too.

$$\underline{Me} + nH_3O^+ \rightleftharpoons Me^{n+} + nH_2O + \frac{1}{2}\, nH_2 \qquad (23)$$

$$\underline{Me} + nH_2O + xOH' \rightleftharpoons (Me/OH/_{n+x})^{x-}, + \frac{1}{2}\,(n+x)H_2 \qquad (24)$$

The mass action law is valid for their solutions and consequently, on changing the OH'-concentration respectively the activity, their hydroxides can be precipitated:

$$Me^{n+} + nOH^- \rightleftharpoons Me/OH/_n + xOH' \rightleftharpoons (Me/OH/_{n+x})^{x-} \qquad (25)$$

n = valence
n+x = co-ordination value in the alkaline medium
If the element in question is aluminium, its alkaline solution is called aluminate liquor.

As it can be seen from the equation (25) no solution of optional OH' to $(Al/OH/_4)'$ ratio can be produced because, if the OH'-concentration (activity) falls below a certain value the decomposition of the $(Al/OH/_4)'$ commences.

In order to characterise the aluminate solutions apart from their concentration the OH' to $(Al/OH/_4)'$ ratio should be known as well. This may be expressed in several manners, it should be agreed how to make one's choice.

In the alumina industry sodium hydroxide solution is used for the dissolution of the aluminium content of bauxite. In the course of precipitation the total aluminium content of the solution cannot be completely be separated. Hence the liquor comprises two main compnents notably the sodium hydroxide and the sodium aluminate. In addition, the liquor becomes carbonate--ferous by the time due to the carbonate content of the ore and the carbon dioxide picked up from the air.

Though the silicates are hard to dissolve in aluminate liquors from the point of view of technology the silicate content is also placed among the main components along with the contaminating organic substances.

Terminology

When evaluating the analytical data of the aluminate solutions, misunderstanding may arise from the non-uniform denomination of the individual components.

Substances which are dissolved in the plant aluminate liquors are given in Table 3.6.

Though the solution comprises ions nevertheless the oxidic composition is established in general. Denominations adopted in the alumina production technology are as follows.

Caustic soda as $Na_2O_{caust.}$

OH-alkalinity of the solution representing the sum of OH^- and the fourth dissociating OH of $(Al/OH/_4)^-$ expressed as Na_2O.

Soda as Na_2O carbonate

CO_3''-content of the solution expressed in Na_2O.

Alkaline soda as Na_2O_A

The amount of Na_2O equivalent to all aklaline hydrolyzing anions.

Total soda as Na_2O_T

Total Na^+-content of the solution expressed as Na_2O.

$\underline{Al_2O_3}$ is the aluminium content of the solution expressed in Al_2O_3.

Caustic molar ratio $\alpha_{caust.}$

The ratio of caustic Na_2O moles to Al_2O_3 moles in 1 liter solutin:

$$\alpha_K = \frac{\dfrac{Na_2O_{caust.}\ g/l}{62}}{\dfrac{Al_2O_3\ g/l}{102}} = 1.645\ \frac{Na_2O_{caust.}\ g/l}{Al_2O_3\ g/l}$$

It should be noted that in the American technical literature and in the practice, too, caustic soda ($Na_2O_{caust.}$) is expressed in terms of $Na_2CO_{3\ caust}$ and similarly all other components given in Na_2O. The conversion may be made by using the factor:

$$\frac{Na_2CO_3}{Na_2O} = 1.71$$

$Na_2CO_{3\ caust} = 1.710.Na_2O_{caust.}$ and

$Na_2O_{caust.} = 0.585.Na_2CO_{3\ caust}$, respectively.

Components of Plant Aluminate Liquors

Table 3.6

Na^+	OH^-	Na_2O caustic	$Na_2O_{caust.}$
	$(Al/OH/_4)^-$	Na_2O carbonate soda	$Na_2O_{carbonate}$
	CO_3^{2-}	Na_2O_{total}	Na_2O_T
	SiO_3^{2-}	Al_2O_3	$Na_2O_{titrable\ total\ alkalinity}$
	organic anions	SiO_2	
		$C_{org.}$	
(K^+)	PO^{3-}	P_2O_5	
contaminants	VO_4^{3-}	V_2O_5	
	F^-, etc.	F, etc.	

The molar ratio used is given by the term M_R.

Further on the oxidic terms and the $\alpha_{caust.}$ concept will be used.

For the soda and salt content, respectively, of the aluminate solutions the terms of

$$\text{soda level} = \frac{Na_2O_{carbonate}}{Na_2O_{caust.} + Na_2O_{carbonate}} \cdot 100 \quad (\%) \quad \text{and}$$

$$\text{salt level} = \frac{Na_2O_T - Na_2O_{caust.}}{Na_2O_T} \cdot 100 \quad (\%), \text{ respectively,}$$

are used.

Chemical Analysis of the Main Components

The determination of caustic soda ($Na_2O_{caust.}$) content is made by acid standard solution. The interfering anions are previously precipitated by Ba-salt solution and a complex former is used (tartarate, gluconate) during the titration in order to avoid the precipitation of $Al(OH)_3$ (47, 48).

For the measurement of carbonate soda ($Na_2O_{carbonate}$) the separated $BaCO_3$ precipitate may be used which is dissolved in a known amount of excess acid solution. After having CO_2 boiled off the amount of acid equivalent to the carbonate content can be titrated by NaOH standard solution. The distillation gas volumetric method may also be used (24).

For the measurement of the alkaline soda (Na_2O_A) the soda salts are converted to Na_2CO_3 by NH_4HCO_3. The aluminium content of the solution is the component that makes the conversion possible and precipitates from the solution at the same time.

$$2\mathrm{Na(Al/OH/_4)} + \mathrm{NH_4HCO_3} = \mathrm{Na_2CO_3} + 2\mathrm{Al(OH)_3} + \mathrm{NH_3} + \mathrm{H_2O} \qquad (26)$$

$$\mathrm{Na_3PO_4} + \mathrm{Na(Al/OH/_4)} + 2\mathrm{NH_4HCO_3} = 2\mathrm{Na_2CO_3} + \mathrm{AlPO_4} + 2\mathrm{NH_3} + 4\mathrm{H_2O} \qquad (27)$$

For the measurement of the total soda (Na_2O_T) the ion exchange method can be used.

The measurement of the Al_2O_3 can be made by the reaction of making complex (EDTA) or by the potentiometric titration. (See Chapter 7.)

The thermometric titration is a very fast method for the measuerement of the caustic soda ($Na_2O_{caust.}$) and Al_2O_3-content.

$$\begin{array}{l} \mathrm{Na_2O\ caust} \\ \left.\begin{array}{r} \mathrm{NaOH} \\ \mathrm{Na\left[Al(OH)_4\right]} \\ \mathrm{Tart^{2-}} \end{array}\right\} + \mathrm{H^+} \begin{array}{l} \longrightarrow \mathrm{Na^+ + H_2O} \\ \\ \longrightarrow \mathrm{Na^+ + H_2O + Al(OH)_3\ Tart^{2-}} \end{array} \qquad (28) \end{array}$$

$$\mathrm{Al_2O_3} \qquad \mathrm{Al(OH)_3\ Tart^{2-}} + 6\mathrm{F'} \longrightarrow \mathrm{AlF_6^{2-}} + \mathrm{Tart^{2-}} + 3\mathrm{OH^-} \qquad (29)$$

The thermometry (for caustic Na_2O and Al_2O_3), as well as the spectrophotometry (for CO_2) is used in the Gardanne plant for the automatic measurement of the aluminate liquors. 10 to 20 samples can be analyzed hourly by this way (49).

The determination of SiO_2-content can be performed by the spectrophotometric method by the measurement of the colour intensity of the reduced Si-Mo heteropoly acid.

For the determination of the organic contaminants the peroxi-bisulfate reaction catalyzed by silver ions is used and the amount of CO_2 equivalent to that of the organic material is measured (42).

In addition the individual organic components may also be measured by means of the gas chromatography.

Investigation of the Contaminants

Of the contaminants of the aluminate liquors the determination of iron, fluorine, vanadium, phosphorus, gallium, zinc, sulfate, chloride and molybdenum is of importance. For the reason of calculation the contaminants of the liquors are also established in terms of oxides.

Determination of the Fe_2O_3-Content of Aluminate Solutions

The iron content of the aluminate solutions contaminates the alumina. During the precipitation about 80 to 90 % of the iron content of the liquor passes into the alumina hydrate.

The solutions comprise partly finely distributed colloidal size floating iron compounds, partly dissolved iron due to the high OH^--concentration.

It is difficult to differentiate between the irons of two origin because due to the small size the clean-cut elimination of the floating iron compounds by filtration is hard to perform.

The iron content expressed in terms of Fe_2O_3 is in the magnitude of mg/l thus for its determination primarily the spectrophotometric methods can be used. The contaminants (e.g. organic compounds, F^-) are more or less interfering with the determination. Of the spectrophotometric methods for the measurement of iron the SCN^- (rhodanide) and the o-phenantroline reaction is used. Concerning the realization of the reaction and the interfering effects several references are available (e.g. 1.).

As per our investigation, good results were achieved when having transferred the iron along with some kind of collector from the solution into a precipitate and the iron content of the latter had been measured. For collector ZnS made by the reaction of Zn-salt and Na_2S is used and it is recommended to adopt the spectrophotometric reaction and the measurement of the colour intensity of the iron-thioglycolic acid complex.

Fluoride content of the strong liquor can become enriched to the magnitude of g/l. As already dealt with in Chapter 8, major part of the fluoride content of bauxite gets into the process circuit. The aluminium content interferes also with the determination of fluoride content of liquors, hence either volumetric or spectrophotometric method were adopted the previous separation by distillation (Willard-Winter) would be necessary.

It is more faster if the fluoride content of liquors is measured by a fluoride-selective electrode (i.e. Orion 94-09, Radelkis OPF-7111 type). In solutions comprising also aluminium the determination of the fluoride ion concentration is restricted due to the formation of alumino-fluoro-complexes because the electrode measures only the free F^--ions. There is a further interfering effect in the presence of silica due to the formation of SiF_6^{2-}-complex. A complex former which displaces the fluoride from the aluminium complex does not interfere with the operation of the electrode thus enabling the measurement beside the aluminium. Edmond (50) and Ingram (51) had used citrate ions as complex formers. Citrate ions up to the concentration of 1M/l do not interfere with the operation of the fluoride-selective electrode. The determinations are made of the ten-fold dilution. The relative error of the measurements is 5 %.

The vanadium content of liquors (for the case of strong liquors $Na_2O_{caust.}$ 180 g/l) can come to 1 g/l. Vanadium salt is removed from the Bayer process circuit by cooling spent liquor or strong liquor (see p. 3-78). Therefore vanadium content of the process liquor circuit should be permanently measured. For the determination of the vanadium content the volumetric potentiometric end point indication method is most accurate having been described in detail in Part 8. The organic substance of the liquor interferes with the titration, therefore it has to be destructed before the determination. The destruction may be carried out either by H_2SO_4-HNO_3 or by $K_2S_2O_8$ in H_2SO_4 medium. After having the organic substance destructed due care should be taken of the complete decomposition of the oxidising agent. Since the chromium content of the liquors is generally less than 1 mg/l the vanadium can be oxidised by $KMnO_4$ and directly titrated/by decomposing excessive $KMnO_4$/ by Fe(II) standard solution. If the chromium content is higher the determination should be made by using the method described for the bauxite. The relative error of the measurement is less than 5 %.

Vanadium may also be determined by means of the spectrophotometry, however, due to the high salt concentration and to the colour of the liquor the application of the differential spectroscopy is expedient.

Phosphorus content becomes also enriched to the magnitude of g/l in the strong liquor and part of it can be removed along with the vanadium salt. If Ca additives are used at the digestion phosphorus content of the liquors considerably decreases due to formation of calcium phosphate.

Phosphorus content of liquors is mainly measured by ammonium molybdate as molybdenum-blue. The measurement can be directly performed of the ten-fold dilution solutions.

The gallium content of the various liquors of the process circuit is of primary importance from the point of view of the recovery of gallium. The equilibrium level of gallium in the aluminate liquors ranges 120 to 140 mg/l, and 190 to 200 mg/l in strong liquors, respectively. The gallium getting into the process circuit mostly contaminates the hydrate. Gallium can be measured chiefly by means of the impulse polarographic method apart from the spectrophotometric one described in Chapter 9. The deposition velocity of gallium is generally very low in the various basic solutions in either acidic or alkaline medium. If, however, the reduction of the gallium-rhodanide complex is performed in the 5 to 6 mole high ion strength electrolite, the reaction becomes accelerated to such an extent that the diffusion gets controled and thus a fairly defined polarographic scale is obtained which is suitable for the measurement of the concentration. The evaluation is made by an additive method. Variation coefficient of the method is 2.

For the determination of zinc content of liquors the AAS is the best method to be selected. When acidified the liquors can be directly atomized in the AAS-unit.

Molybdenum content of strong liquors may exceed 200 mg/l (see Chapter 9.). The determination of molybdenum may be carried out by means of the AAS method or after forming and separating a precipitate (α-benzoinoxim) by means of the polarography, too.

In favour of the removal of the ballast salts the measurement of sulfate content of liquors is also important. The amount of Na_2SO_4 in the strong liquor ($Na_2O_{caust.}$ 180 g/l) may attain at the magnitude of 0.4 to 0.6 g/l.

The determination of the sulfate content is made by the gravimetric method (acidifying and precipitating as $BaSO_4$).

The liquors comprise also chloride ions in some cases. This can be volumetrically measured after the destruction of the organic substance. Excessive amount of $AgNO_3$ standard solution of known titre is added to the nitric acidic solution. AgCl precipitates. The excessive $AgNO_3$ standard solution is back-titrated by KSCN standard solution. Fe(III)-salt is used as an indicator.

For the determination of the main components and trace contaminants of the aluminate liquors X-ray-fluorescent methods are also known (52).

13. DETERMINATION OF THE CONTAMINATING COMPONENTS IN ALUMINA

A number of contaminating components from the caustic solution segregate simultaneously with the alumina hydrate separation in the Bayer alumina producing process, or they link to the large-surface precipitates (sorption) and cannot be totally removed even by washing. Certain contaminating components may get into the alumina during calcination (e.g. sulphur). The contaminating components of alumina exercise disadvantageous influence on the utility of aluminium in the aluminium metallurgy and deteriorate its properties in industrial applications. From the aluminium metallurgical poiunt of view certain impurities are disadvantegeous because they contaminate the metal while separating along with the aluminium during the electrolysis. Two of the most critical impurities are Fe_2O_3 and SiO_2. Both TiO_2 and V_2O_5 are undesirable contaminating components when producing conductivity grade metal.

Some contaminating components Na_2O, P_2O_5 for example have an unfavourable influence on the electrolysis, as Na_2O modifies the cryolite-melt's molar ratio ($3NaF/AlF_3$) toward the caustic direction. Fig. 3.7 gives a survey about the contaminating components of alumina. Examining the figure it turns out that Na_2O is the major contaminating component of the alumina if we leave out of consideration the here not indicated moisture content (which can be measured by a loss of mass at 300 °C and loss of mass at 1100 °C). A part of this Na_2O content, the so-called water-soluble Na_2O originates from the insufficient washing of the caustic solution. Recently the determination of the total Na_2O content (water-soluble+combined Na_2O) is general. The sequence of the contaminating components in the Fig. 3.7 provides at the same time their order of undesirability from a metallurgical point of view.

The analytic determination of the contaminating components of alumina is essential first of all because of plant supervision reasons and the marketability of the finished product.

Appart from the classical chemical analytical methods mainly spectral analysis, AAS and X-ray spectrometry are used for the determination of the alumina's contaminating components. Sometimes electroanalytic (polarographic) methods are applied to determine certain components like Cu and Zn. Activation analysis methods may be suitable in certain cases (e.g. P_2O_5). Single-purpose equipments working on the principle of IR spectrophotometry (after burning) are also used to determine the carbon and sulphur content of alumina. Not the exact quantitative determination of contaminating components is the aim of the mass spectrometric tests of aluminas but we rather strive after a semi-quantitative comparative investigation concerning all the elements. This method is mainly used recently in the research work. Table 3.7. gives a summary of the various methods for the determination of contaminating components of the alumina.

Classical Chemical Methods

Chemical tests have to be carried out on samples prepared always according to the instructions of chapter 6.

As mentioned before the dissolution or attack of the alumina does not mean an easy task. The most frequently used methods for attack can be divided into two groups:
- method by alkaline fusion
- method by acid attack under pressure.

A great number of variations of the alkaline-fusion method is used. The oldest one is the fusion with soda-borax mixture (53). Today instead of borax boric acid is used. This is recommended by the ISO standard as well (54).

Methods for the Determination of the Contaminating Components of Alumina

Table 3.7

COMPONENTS

	wet. chem.	Em. spectr.	X-Ray spectr.	Flame photom.	AAS	Polarography	IR spectr.
Na_2O total		+	+	+			
Na_2O w.sol.	+						
Fe_2O_3	+	+	+				
SiO_2	+	+	+				
TiO_2	+	+	+				
V_2O_5	+	+	+				
P_2O_5	+						
CaO		+	+		+		
ZnO	+		+		+	+	
SO_3	+		+				+
Mn_2O_3	+	+			+		
Cr_2O_3	+	+					
CuO	+					+	
F	+						
C							+
MgO		+			+		
NiO	+	+			+		
Ga_2O_3	+	+					
Cl	+						
B_2O_3	+	+					
Al_2O_3			+				

Methods →

For the determination of alkali metals (Na_2O), Li_2CO_3, H_3BO_3 + Li_2CO_3, $Li_2B_4O_7$ in some cases H_3BO_3 or B_2O_3 is used as [illegible] agent.

Experiments have been carried out since the 50-ies (55) dealing with the acid attack of alumina under pressure in a sealed glass tube between 200-300 °C. Special difficulties in this case arise first of all with the material of the tube itself because even the components of boron-silicate glass may dissolve (56). Recently steel attacking boms with heat resistant plastic lining are applied generally, nevertheless it needs to be thoroughly investigated, whether or not a component reacts with the plastic during the attack. The run of the attacks under pressure needs a long time, 12-16 hours as a rule, but their great advantage is that further processing can be done with a relatively small salt-concentration. This method for attack is mainly used in case of AAS and solution Emission Spectrometric testings.

The C and S content of the alumina can be determined very quickly and with sufficient accuracy in special combustion equipments (e.g. Leco CS-46). If we heat the alumina in an oxygen flow its carbon will burn into CO_2 or CO, its sulphur into SO_2. Accelerating agents are added to help the combustion. The CO, CO_2 and SO_2 content of the combustion product is measured by IR detectors. If oxygen alone gets into the measuring cell the total energy of the IR radiation will reach the detectors. The combustion products (CO_2, CO, SO_2) in the measuring cell absorb energy during the test and this energy is proportional to their concentration. This causes a decrease in the energy reaching the detectors and this diminished energy is measured by means of the detectors. Taking the amount of the charge into account the C and S quantity is indicated on the DVM in % after rectifying, amplifying and linear transforming of the signal. The evaluation of the results is carried out by comparison with reference standards.

The C and S content of the alumina can be determined with 4-7 % error by means of this method: within a very short time approximately 2 minutes.

There are internationally standardized methods at our disposal today for the determination of the most important contaminating components of the alumina, which have been tested and verified several times. We give a summary of them in see Table 3.8.

Spectrophotometric methods are applied in most cases (e.g. SiO_2, Fe_2O_3, TiO_2).

Sometimes an extraction process preceeds the spectrophotometry because of the small concentrations (e.g. V_2O_5, P_2O_5, ZnO). AAS method is prescribed by the standards a couple of times (e.g. CaO, MgO, ZnO, MnO). In the case of fluoride and boron - because of the interfering effect of the aluminium - a distillation separation is necessary.

We wish to stress that the fluoride content of the alumina in the range of a 0.01 % order and the B_2O_3 content being even less, have no harmful effect from a metallurgical point of view; their determination is required rather because of their role as mineralizators added to the alumina (AlF_3, B_2O_3).

Dissolution methods are sometimes applied for alumina analysis. Production plants used to test the soluble Na_2O content regularly. The principle of the method is that the Na_2O content adhered to the surface dissolves when boiling with water and can be measured by titrating with acids. The widespread application of the flame-photometers has forced back the former method; today the measuring of the total Na_2O content may be regarded as general. The sulphur content of aluminas can be determined in a similar way by means of dissolution. The sulphur content in the alumina is mostly present

Standard Methods Used for the Analysis of Aluminium Oxide

Table 3.8

#	Component	Principle of the determination	Method	Field of application Range	ISO Number
1.	Loss of mass at 300 °C	Drying of the test portion at 300 °C for 2 h and determination of loss of mass			803-1976
2.	Loss of mass at 1000 °C and 1200 °C	Ignition of two test portions previously dried at 300 °C one at 1000 °C and the other at 1200 °C, for 2 h			806-1976
3.	Na_2O	Fusion of the test portion with mixture $Li_2CO_3+B_2O_3$ or $Li_2CO_3+Li_2B_4O_7$. Dissolution in HCl. Aspiration of the solution into a flame	Flame emission spectrophotometric		1617-1976
4.	Preparation of solution for analysis	Alkaline fusion method			804-1976
5.	Fe_2O_3	Alkaline fusion, reduction of iron(III) to iron(II). Formation of the iron(II)-1.10-phenanthroline complex. pH 3.5-4.2. Photometric measurement at wavelength 510 nm	Spectrophotometric	> 0.005 %	805-1976
6.	SiO_2	Alkaline fusion, formation of the oxidized molybdosilicate, selective reduction. Photometric measurement at wavelength of 815 nm	Spectrophotometric	0.005-0.025 0.025-0.25	1232-1976
7.	TiO_2	Alkaline fusion test solution. Formation of the titanium-diantipyryl-methane complex. Photometric measurement of the coloured complex at a wavelenth of 420 nm	Spectrophotometric	> 0.001 %	900-1977
8.	V_2O_5	Alkaline fusion, test solution, oxidation to V(V). Formation of vanadium N-Benzoyl-N-phenylhydroxyl--amine complex. Extraction of the violet coloured complex. Photometric measurement at a wavelength of 524 nm	Spectrophotometric	0.0003-0.016 %	1618-1976
9.	P_2O_5	Preparation of solution from a test portion by alkaline fusion and by dissolution in nitric acid (pH 2). Formation of the phosphomolybdic complex. Extraction by 2-methylpropan-1-Ol. Reduction of the complex by $SnCl_2$ in the organic phase. Spectrophotometric measurement at a wavelength of 730 nm	Spectrophotometric	> 0.0005 %	2829-1973
10.	Preparation of solution for analysis	Method by hydrochloric acid attack under pressure			2073-1976

Table 3.8 (cont.)

#	Component	Principle of the determination	Method	Field of application Range	ISO Number
11.	ZnO	Alkaline fusion, treatment of the fused mass with HNO_3. Separation of the Zn in the form of thiocyanate by extraction with metyl-isobutyl ketone. Re-extraction with HCl solution. Formation of the PAN-zinc complex. Extraction of the PAN-zinc complex with chloroform and photometric measurement at a wavelength of 560 nm	Spectrophotometric		R 2072-1971
		Dissolution by attack with HCl under pressure aspiration of the solution in acetylene air flame measurement of the absorption of the 213.8 nm line emitted by zinc hollow-cathode lamp	AAS	>0.002	2076-1976
12.	MnO (Mn)	Dissolution with hydrochloric acid under pressure. Aspiration of the solution in an air/acetylene flame and measurement of the absorption of the 279.5 nm line emitted by a manganese hollow cathode lamp	AAS	0.00026-0.0065 (Mn 0.0002--0.005)	3390-1976
13.	CaO	Alkaline fusion. Precipitation of the calcium in alkaline medium with naphthyl-hydroxamic acid solution. Spectrophotometric measurement of the excess of naphyl-hydroxamic acid at wavelength of 400 nm	Spectrophotometric	>0.01 %	
		Dissolution by attack with HCl under pressure. Addition of Na-ions to stabilize the promotion of the emission of Ca and lanthanum ions or triethanolamine to increase the sensitivity. Aspiration of the solution into acetylene dinitrogen monoxide flame and measurement of the absorption 422.7 nm line emitted by a calcium hollow--cathode lamp. CaO contents greater than 0.03 acetylene/air flame can be used	AAS	>0.003 %	2063-1976
14.	F	Dissolution by attack by H_2SO_4 under pressure. Separation of the fluorine by distillation. Formation of the blue coloured complex between F and alizarin complexone lanthanum chloride. Spectrophotometric measurement of the complex at a wavelength of 620 nm	Spectrophotometric	>0.003	2828-1973
15.	B_2O_3	Dissolution with H_3PO_4, separation of B by distillation as methyl borate. Formation of the red coloured complex between B and curcumin. Spectrophotometric measurement of the complex at a wavelength of 550 nm	Spectrophotometric	>0.0006	2865-1973

in the form of sulphate, which is quantitatively dissoluble with Na_2CO_3 or $(NH_4)_2CO_3$. After dissolving the SO_4^{--} being in solution it can be separated with $BaCl_2$. Rather large 10-30 g charges of samples are required to make possible the measurement of the small $BaSO_4$ quantity.

Spectral Analysis of the Alumina

The long duration of wet assay of aluminas made the production plants turn toward instrumental measurements. Spectral analysis seems to be one of the most suitable methods for this purpose. Alumina has to be mixed up with graphite powder in a 1:2 ratio as the first step. Then the mixture is evaporated by direct current arch anodic excitation with a graphite cup electrode. The determination is done by quartz spectrograph in the ultra violet spectral range. The preferred spectral line pairs are measured by photometry and the concentration of the individual contaminating components is determined from evaluating curves plotted on the basis of the analysed standard series.

Contaminating components tested regularly by the help of spectral analysis are: Na_2O, SiO_2, Fe_2O_3, TiO_2, V_2O_5, CaO. In the case of MgO, BeO and Ga_2O_3 special reference standards are required, which can be made by mixing spectral-clean Johnson-Matthey oxides with natural alumina.

It seems to be expedient to use the total evaporating method in the analysis of alumina samples if we want to eliminate the errors originating from the crystal structure of alumina (αAl_2O_3, βAl_2O_3). The average error of the spectral alumina analysis is about 5 % relative error. Flame photometry guarantees more accurate results as a rule, in case of determining Na_2O content.

X-Ray Spectrometry

X-Ray spectrometry is specially adequate for the determination of the contaminating components of the alumina. It seems to be expedient to carry out the determinations on compressed pastille samples, as the concentration of the contaminating components is low. This technique is suitable for measuring SiO_2, Fe_2O_3, TiO_2, CaO, ZnO, V_2O_5, SO_3. The relative error of the method is about 2-5 %. Sodium is the lightest element generally attempted using a conventional X-Ray fluorescence-spectrometer, and the possibility of its accurate determination at low concentration was considered doubtful. In order to achieve best conditions for the determination of Na thallium acid phthalate (TAP) crystal was purchased.

Greater accuracy than with the wet assay method can be achieved when measuring the direct Al_2O_3 content of alumina if beads, fused with $Li_2B_4O_7$, are used. Relative error as small as 0.2 % can be obtained by this method (57).

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