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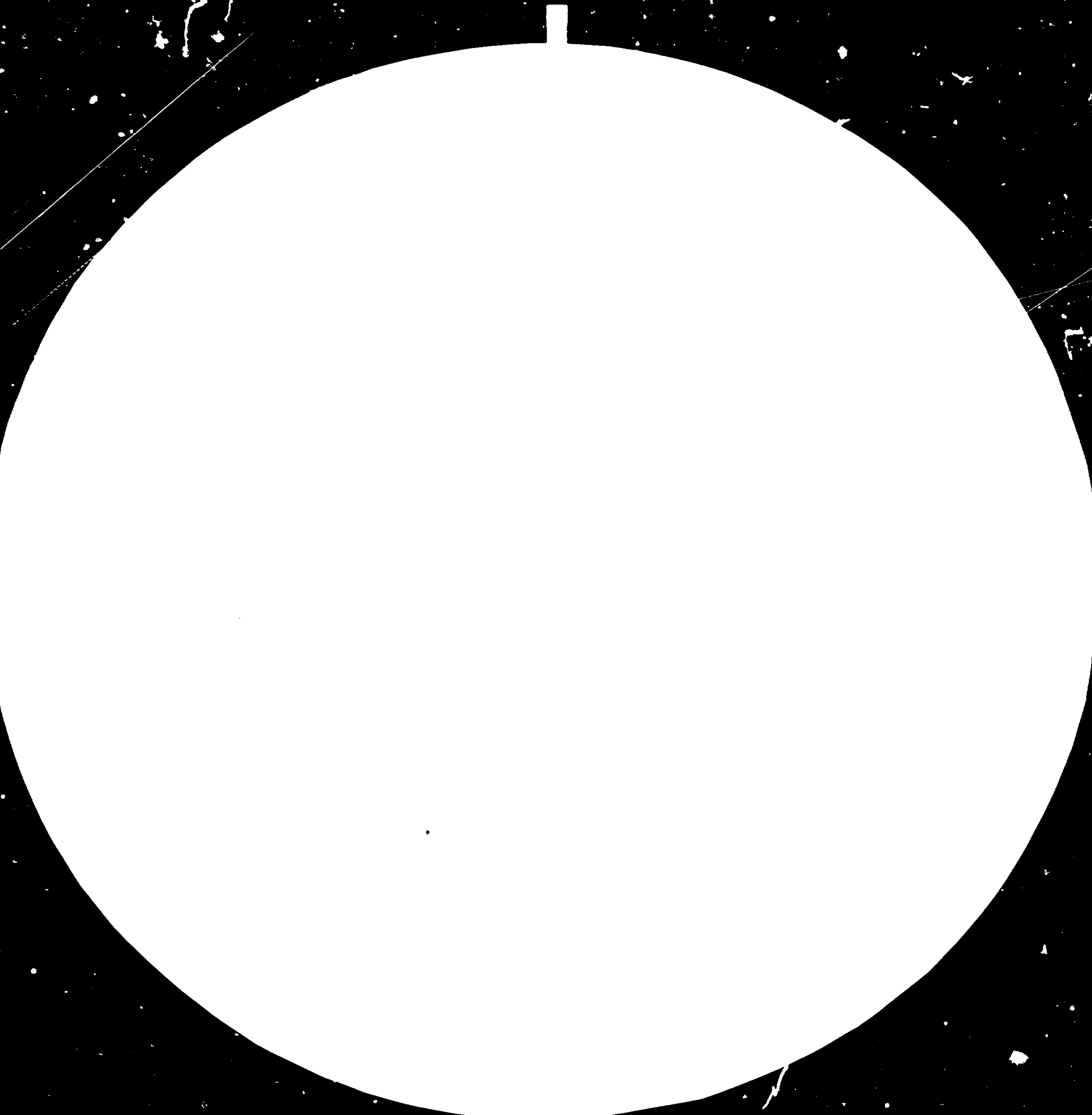

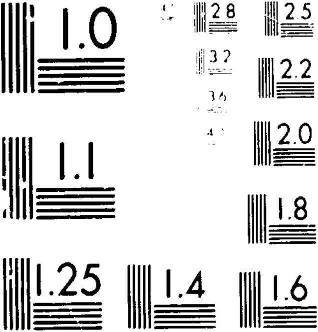

MICROCOPY RESOLUTION TEST CHART

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United Nations Industrial Development Organization

GROUP TRAINING IN PRODUCTION OF ALUMINA.

VOLUME 8.

MANUAL FOR LABORATORY.

ALUTERV-FKI

BUDAPEST, JULY 1979

VOLUME 8

MANUAL FOR LABORATORY

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1. INTRODUCTION

GENERAL ASPECTS OF THE LABORATORY PRACTICES

The present volume can be considered as a continuation and complement of the study "Analytical Methods for Testing Bauxite, Alumina and Intermediate Products" (UNIDO/ITD. 171.) published by UNIDO in 1973. The material of the practices is based on the knowledge of the first seven volumes of "Group Training in Production of Alumina, 1979".

At compiling the laboratory practices the aim was to demonstrate the most important instruments, measuring and evaluation methods needed to bauxite evaluation from the point of view of Bayer process, taking into consideration that the chemical analyses, the mineralogical, petrolcgical and physico-chemical investigations should have their share beside the technological investigations, corresponding to the principles laid down in Volume 6, just as an up to date technological evaluation can not be imagined without using modern material science investigations.

Laboratory methods applied to technological evaluation of bauxites can be classified into the following three groups from the view-point of their general use and standardization:

1. International standardized methods (ISO standards)
2. Standards and evaluating methods accepted between different countries or companies (national standards)
3. Non standardized methods used by certain companies in-doors.

It is evident that in the first place the chemical analytical methods used for quality control of raw material (bauxite) and commercial product (alumina) are prescribed in international standards. The application of certain quality control methods is usually layed down in the quality requirements of commercial contracts.

For the technological investigations and for some mineralogical (quantitative phase analysis ,electronic ray methods) and physico-chemical investigations, not only the standards but the detailed review of the methods, too are missing from the literature.

The reason is that beside the difficult standardisation, these methods have mostly a "Know how" character.

We tried to collect the laboratory practices in a logical order and to give such a detailed description that the secondary school qualified staff of a target-laboratory being established in any country could master them.

The theoretical principles of the measurements are described in the previous volumes, so we disregard their repetition.

2. X-RAY DIFFRACTOMETRY (XRD)

PRINCIPLES

The X-ray diffractometric phase analysis of powder mixtures is based on two independent principles:

a) An X-ray diffractogram of a phase (peak positions and relative intensities) is uniquely characteristic for it. This allows a qualitative phase analysis.

b) I_{ij}, the integrated intensity of the j-th line of the phase i relates to its weight fraction (x_i) according to the equation

$$I_{ij} = \frac{K_{ij}\; x_i\; R_{ij}}{\varrho_i\; \mu_T} \tag{1}$$

where:

K_{ij} : is a constant depending on the characteristics of the apparatus, the X-ray wavelength and the structure of component i,

$_i$: is the density of component i,

μ_T : the mass absorption coefficient of the specimen including component i, i.e. $\mu_T = \sum x_j\, \mu_j$. While μ_T depends on x_i, I_{ij} is not strictly propertional to x_i. The deviation is usually referred as "matrix effect".

R_{ij} : is the relative intensity of the j-th line in the units of the strongest one.

The various methods of X-ray diffractometric phase analysis all use different forms of eq. (1).

ABSOLUTE INTENSITY METHOD

When only one component is sought and its measured intensity is referred to a scale corresponding to pure component i, eq. (1) has the following form:

$$I_{ij} / I_{ij}(x_i=1) = \mu_i/\mu_T \; x_i \qquad (2)$$

where only μ_T is unknown.

Depending on the difference between the mass absorption coefficient of the phase i and the remaining part of the sample convex, concave or straight calibration curves are applied. This method needs numerous, complex and variable calibration for multicomponent systems, so it is not worth applying in that case. However, it is the fastest method for determination of alpha corundum content of aluminas. The mass absorption coefficient of different aluminas is very close to each after, thus the calibration curve is a straight line.

INTERNAL STANDARD METHOD

The absorptive characteristics of the sample can be dropped out from eq (1) relating I_{ij} to the 1-th line intensity of the phase s, I_{s1}:

$$I_{ij}/I_{s1} = \frac{K_{ij} \, \rho_s \, x_i \, R_{ij}}{K_{s1} \, \rho_i \, x_s \, R_{s1}} \qquad (3)$$

The common factor μ_T was cancelled from eq. (3). Component s is an internal standard to which component i is referred. As K_{ij} contains apparative parameters as multiplying factors $K_{ij}(K_{s1}=k_i)k_s$, where k_s depend only on the phases i and s. The k factors are usually referred to as intensity conversion factors (ICF-s). If one has a calibration curve: I_{ij}/I_{s1} versus

x_i/x_s, it is necessary only to mix the sample with a known amount of the standard and measure the relative intensities. The weight fraction of the phase i can be read from the calibration curve. As the absorption coefficients have been eliminated, eq. (3) always presents a straight calibration curve which can be characterised by its slope. It is sometimes more advantageous to dilute the specimen with known amount of the component, whose concentration is to be determined. In this case the amount (and even the identity!) of the standard component s need not be known ("solution with unknown method"). The intercept of the line fitted to the relative intensity versus added-unknown-points with the axis of added unknown gives the fraction of the unknown component in the original sample.

QUANTITATIVE XRD ANALYSIS WITHOUT STANDARDS

In the case of n unknown component in the specimen, one has at least n equations of type (1), but only (n-1) measured relative intensities and equations of type (3). Only if the qualitative analysis is complete, one has a normalisation condition for concentrations: $\sum_j x_j = 1$, which can be used for n-th equation. The solution of the linear equation system has a symmetrical form:

$$x_i = \left(\frac{k_i}{I_i} \sum_{j=1}^{n} \frac{I_j}{k_j} \right)^{-1} \qquad (4)$$

COMPLEX PHASE ANALYTICAL METHOD FOR BAUXITES AND RED MUDS

All methods mentioned above require the knowledge of the calibration curves or ICF-s, or at least samples from the pure unknown component with the same ICF as in the sample. In case of minerals, and especially of bauxites, a very wide distribution of ICF-s was found, depending on the geohistory of the ore.

The same is valid for the technological materials of different processing. The best in this case is to minimize the role of ICF-s in the phase analysis. The computer version of this algorithm is detailed in the theoretical lectures (Vol.4., Chapter 2.).

The purpose of this test is to introduce in the different methods and problems of XRD (sample preparation, selection of optimum measuring parameters of the diffractometer, etc.), qualitative and quantitative evaluation of diffractograms of artificial mixtures, and application of the complex method for bauxite phase analysis, to check the tehcnological steps by qualitative evaluation of red muds, and to qualify aluminas by quantitative determination of their alpha corundum content.

EXPERIMENTAL PART

SAMPLE PREPARATION

Specimens are made from the ground sample (having a particle size of less than 63 /um by a hand press in a thin aluminium sample holder (Fig.8.1). Put a piece of abrasive paper on the press tool and fit the sample holder on the metal peg. Powder the sample on the rough surface of the abrasive paper and smooth it with the spatula. Lay it on the counterpart of the press tool, slip the whole tool into the press and tighten it. Open the press and the tool and cover the back of the sample by a flexible cover-plate. Slip the sample holder into the magazine and crack it in cautiously (Fig. 8.2). Make a record of the sample position and identity, fill in the form.

DESCRIPTION OF THE DIFFRACTOMETER SET-UP

The block diagram of a conventional XR diffractometer can be found in the Chapter 2. of vol.4 (see figure 4.14).

Our XRD equipment is based on commercial Philips units, but it has been modified to make serial measurements comfortable. A quick return motor has been mounted on the goniometer (Fig. 8.3.), the chart motion and low angle start of the goniometer has been synchronised so that the half degree markers conincide with the thick lines of the recorder paper (Fig. 8.4.). Additionally a sample selector unit is connected to the automatic Philips sample changer. Two scalers are mounted working in a flip-flop mode not to waste counts during printing time. The printer is replaced by a paper tape puncher to produce diffractometric data for direct evaluation by a computer.

PREPARATION OF THE DIFFRACTOMETER FOR MEASUREMENT

Switch on the X-ray generator, the goniometer supply, the sample changer control unit, the sample selector unit, the high voltage supply of the scintillation detector, the scaler the ratemeter and the counter control unit. Turn on the tap of the cooling water of the generator and the X-ray tube. After one minute waiting, turn the h.v. switch of the generator to the left, and then slowly, gradually turn it to the right, up to 44 kV. Then turn the tube current up to 22 mA. These are the normal operating parameters of our X-ray tubes.

Insert the filled magazine into the sample changer and mount on the gears appropriate for the chosen goniometer speed (the possible combinations are marked in a table on the goniometer). Position the angular limit stops by loosing and tightening the curled screws L (lower limit) and U (upper limit) seen on the Fig. 8.3 . Position the upper side of the vertical limit stop of the sample changer to the groove corresponding to the highest number of sample in the magazine wanted to be measured in the same run. Position the time constant switch of the ratemeter to the highest value (τ), which satisfies the condition:

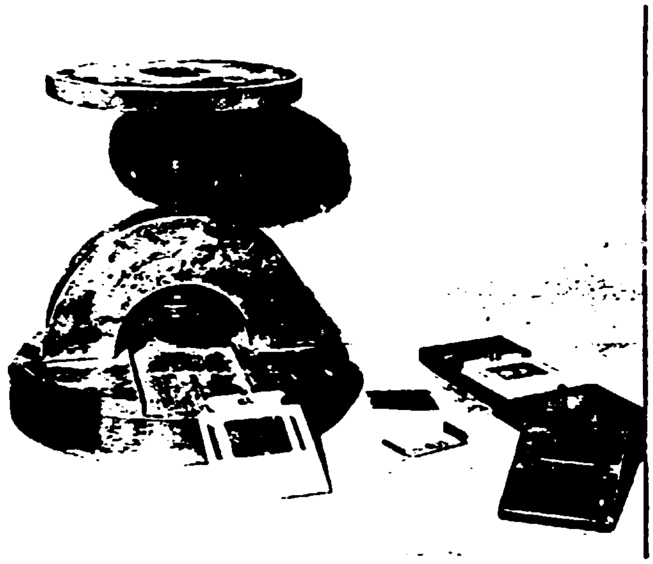


Fig.8.1
HAND PRESS FOR SAMPLE PREPARATION

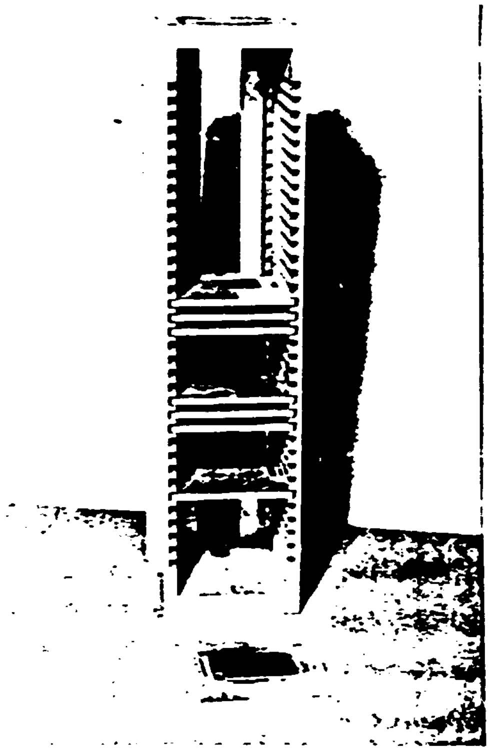


Fig. 8.2
THE SAMPLE MAGAZINE

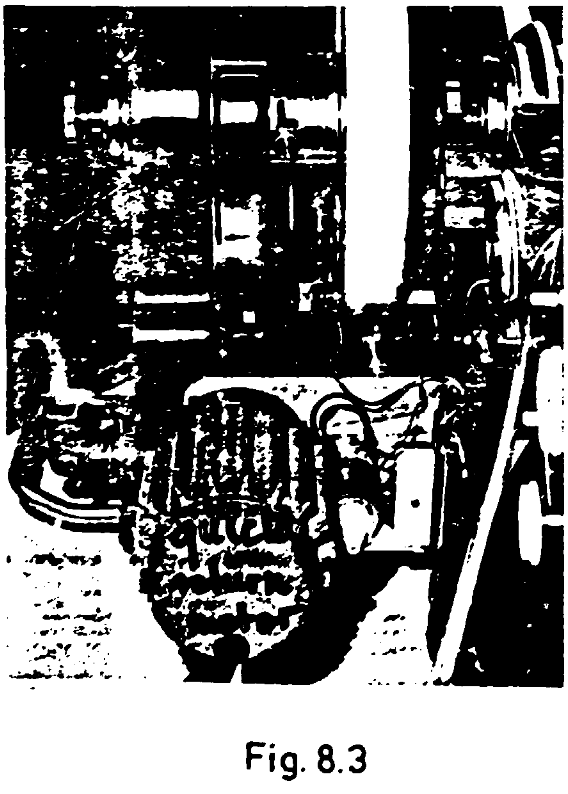


Fig. 8.3

THE MODIFIED VERSION OF GONIOMETER WITH THE QUICK RETURN MOTOR

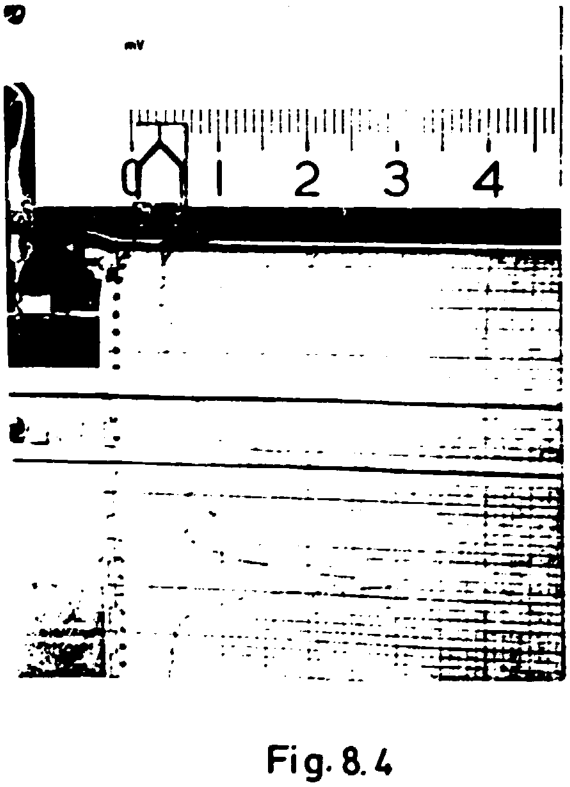


Fig. 8.4

THE MARKERS AND THE THICK LINES OF THE CHART ARE SYNCHRONIZED

$$s \times \tau = 4 \qquad (5)$$

where s is the goniometer speed (degree per minute), τ is the time constant of the ratemeter in seconds. This condition guarantees that peaks will not be overintegrated on the record. The recording may be started by pushing the "START" button on the front panel of the sample changer control unit. Then open the X-ray gate 3 by pushing the button 3 on the generator panel after turning the selectort switch under it to the position "∿". Now the diffractometer set-up is ready for operation.

CAUTION!

The X-ray radiation is dangerous for the human body, especially for the eyes. Please, do not touch the radiation protection between the X-ray tube and the detector. In normal use the equipment is radiationproof.

EXERCICES

QUANTITATIVE DETERMINATION OF THE ALPHA-CORUNDUM CONTENT OF AN ALUMINA SAMPLE BY THE ABSOLUTE INTENSITY METHOD

Prepare four paralel samples from the material and use the 100 % alpha-corundum standard (available in the laboratory) as reference. For the sake of simplicity, put the standard sample into the position 1 of the magazine. Starting the measurement the way described above, take a short record of the reference sample from 23 to 28° (in 2θ) with 1°/min. of goniometer speed. The proposed sensitivity: 1×10^3 cps. Find the line of corundum (a 75 % line with 012 Miller indices) at 2θ-25.6°. Position the lower angle limit stop slightly below 24° and mount the gears on appropriate for 0.5°/min. goniometer operation. Switch on the printer and turn the preset count switch of the scaler to ∞. Preset the measuring time to 100 sec on the timer PW 4261. As soon as the sample has moved in, start the scaler. When it has stoped, reset it and preset the measuring time to 200 sec.

After this measurement count background for 100 sec again. When the next sample has moved in, repeat the whole procedure. The printer automatically reads out the scaler when it has stoped.

Evaluation

The sum of the two counts measured for 100 sec (background values) are to subract from the count measured for 200 sec to obtain the integrated intensity (I) of the corundum peak (see Fig. 8.5.). The ratio of this with respect to the integrated intensity (I_{st}) of the standard (100 % alpha-corundum) gives the fraction of alpha-corundum in the sample.

The statistical error in the concentration

$$\Theta_{(c)} = 3 \cdot \frac{I_{st}\sqrt{I/200/}+\sqrt{I_1/100/}+\sqrt{I_2/100/)}+I(\sqrt{I_{st}/200/}+\sqrt{I_{1st}/100/}+\sqrt{I_{2st}/100/}}{I_{st}^2}$$

is usually less than the reproducibility error in the sample preparation. Calculate the average and the empirical standard deviation of the corundum content for the four parallels by pocket calculator PTK 1030. Please make notes of the parallel concentrations, the average, as well as the statistical and standard deviations.

QUANTIATIVE DETERMINATION OF HEMATITE IN AN UNKNOWN MIXTURE OF HEMATITE-SYLVITE (KCl)-CORUNDUM BY THE "SOLUTION WITH UNKNOWN METHOD"

The unknown mixture (sample "U") with x weight per cent hematite and two additional samples with x+20 and x+40 weight per cent hematite content are available.

Study the diffractogram of the unknown (chart available). Mark and identify the lines of hematite, corundum and sylvite. (Tables are available in the laboratory.) Select the shortest

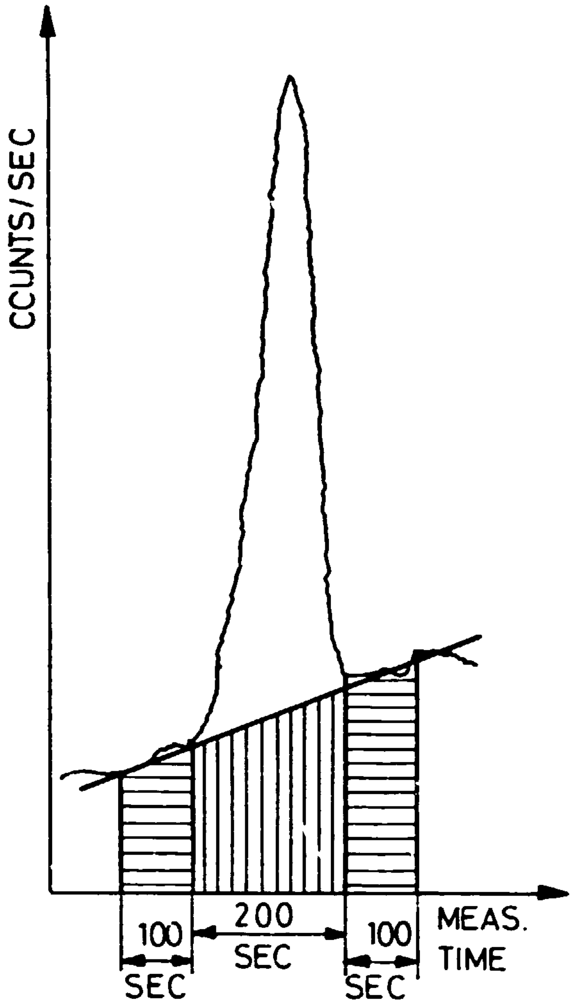


Fig. 8.5
DETERMINATION OF THE ALPHA-CORUNDUM CONTENT

THE JOINT AREA OF THE HORIZONTALLY STRIPED TRAPEZOIDS IS EQUAL TO THAT OF THE VERTICALLY STRIPED

2θ interval in which all three phases have a single, nonoverlapping peak with a pretty high (>30 per cent) relative intensity. Set the angle limits and take a 0.5°/min. record of the three samples ("U", "U+20", "U+40") in the angle interval chosen.

Evaluation

Determine the integrated intensities of the peaks supposing a linear background and estimating the area of the peaks by that of an approaching triangle (see Fig. 8.6.). For the relative intensities of the chosen line of hematite with respect to the chosen line of the standard, the hematite content of the sample is to be determined by the method described in para Internal standard method.

QUANTITATIVE DETERMINATION OF ALL THE THREE PHASES IN SAMPLE "U" WITHOUT STANDARDS

Determine the further necessary peak intensities from the record of the sample "U" by the triangle method. Take the standard intensity conversion factors (relating to corundum) from the JCPDS Index and use the formula (4).

STARTING AN AUTOMATIC SIMULTANEOUS CHART AND PUNCH TAPE-DIFFRACTOGRAM PREPARATION OF A BAUXITE SAMPLE

Set the lower angle limit to 5° and the upper one to 46°, mount on gears for 0.25°/min. operation, switch on the flip--flop mode scalers and the tape puncher. Select the sensitivity as 1×10^{3} cps and an appropriate time constant for the ratemeter, and start recording. The automatic data collecting system prepares the records in an all-night operation.

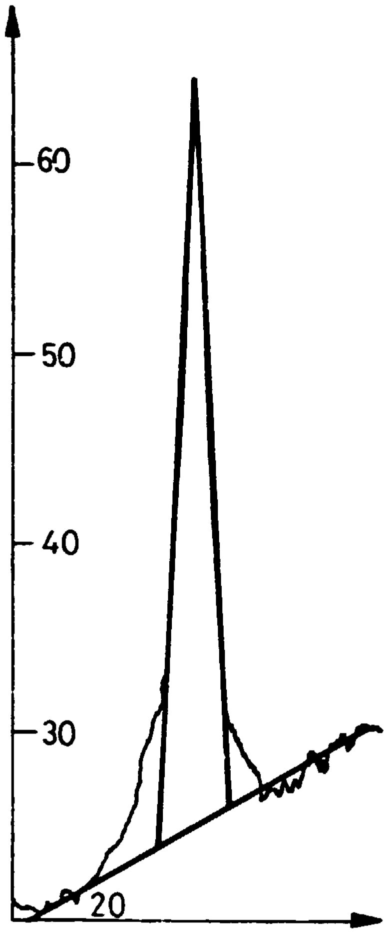


Fig. 8.6

DETERMINATION OF INTEGRATED INTENSITY BY THE TRIANGLE METHOD

QUANTITATIVE ANALYSIS OF A RED MUD DIFFRACTOGRAM BY MEANS OF THE TABLES AND FILES AVAILABLE IN THE LABORATORY

Mark and try to identify the peaks on the chart and make a note of the phases present in the sample. Focus attention to the retained aluminium phases and silicates beside the main red mud phases. Make use of the knowledge of the technological steps (for example lime addition, if any) and data of the chemical analysis available.

QUANTITATIVE PHASE ANALYSIS OF THE BAUXITE SAMPLE (MEASURED PREVIOUS NIGHT) BY THE COMPLEX METHOD DESCRIBED IN CHAPTER 2. OF THE VOL.4.

1. by a "hand evaluation" of the record
2. with the aid of the HP 9830A desc calculator (demonstration)

The following steps of the evaluation are necessary along the lines of exercices 1-5:

a) Complete qualitative analysis making use of the diffractogram chart by means of tables available.

b) Determination of the line shifts (due to foreign atom substitutuion) of goethite, hematite (and to diaspore, calcite or siderite if any) by fitting the anatase 110 line to the right position ($2\Theta = 25.3^{o}$). Correction of the composition according to the calibration curves (line shifts versus mole per cent of the isomorphous substitution) available in the laboratory.

c) Determination of the integrated intensities of the main lines of the phases in the sample by the triangle method and correction for overlapping with the help of the tables of relative intensities.

d) The distribution of oxides for the phases according to the chemical composition of phases (Table 8.1) making use

Table 8.1

CHEMICAL COMPOSITION OF THE PHASES IN OXIDE PERCENTAGES

	Al_2O_3 %	Fe_2O_3 %	SiO_2 %	TiO_2 %	CaO %	MgO %	FeO %	P_2O_5 %	Mn_3O_4 %	CO_2 %	Na_2O %	L.O.I. %
Hematite	1.0	100.0	0	0	0	0	0	0	0	0	0	0
Boehmite	85.0	0	0	0	0	0	0	0	0	0	0	15.0
Cancrinite	32.8	0	38.6	0	0	0	0	0	0	0	26.6	1.9
Sodalite	32.8	0	38.6	0	0	0	0	0	0	0	26.6	1.9
Perowskite	0	0	0	58.8	41.2	0	0	0	0	0	0	0
Goethite	1.0	89.9	0	0	0	0	0	0	0	0	0	10.1
Corundum	100.0	0	0	0	0	0	0	0	0	0	0	0
Gibbsite	65.4	0	0	0	0	0	0	0	0	0	0	34.6
Diaspore	85.0	1.0	0	0	0	0	0	0	0	0	0	15.0
Kaolinit	39.5	0	46.5	0	0	0	0	0	0	0	0	14.0
Portland	0	0	0	0	75.7	0	0	0	0	0	0	24.3
Ca-aluminate	30.9	0	1.0	0	36.4	0	0	0	0	0	0	32.7
Na-titanate	0	0	0	56.3	0	0	0	0	0	0	43.7	0
Ilmenite	0	52.6	0	52.7	0	0	47.3	0	0	0	0	0
Siderite	0	68.9	0	0	1.0	1.0	0	0	0	31.1	0	38.0
Magnetite	0	103.5	0	0	0	0	0	0	0	0	0	0
Lithiophillite	25.3	0	0	0	0	0	0	0	56.8	0	0	17.9
Magnesite	0	0	0	0	0	47.8	0	0	0	52.2	0	52.2
Anatase	0	0	0	100.0	0	0	0	0	0	0	0	0
Calcite	0	0	0	0	56.0	1.0	0	0	0	44.0	0	44.0
Dolomite	0	0	0	0	30.4	21.7	0	0	0	47.7	0	47.9
Quartz	0	0	100.0	0	0	0	0	0	0	0	0	0
Rutile	0	0	0	100.0	0	0	0	0	0	0	0	0
Pyrite	0	66.7	0	0	0	0	60.0	0	0	0	0	33.3
Maghemite	0	100.0	0	0	0	0	0	0	0	0	0	0
Grandallite	33.1	0	0	0	12.1	0	0	41.1	0	0	0	13.7

of formule (4). The relative intensity conversion factors and their standard deviation are given in the Table 8.2 (see. Chapter 4., too.). The evaluation is helped by standard forms with the main bauxit components (Fig.8.7).

e) Recalculation of the phase composition with modified relative intensity conversion factors (but inside the interval marked in Table 8.2) starting from the point d) if the L.O.I., or the sum of the phase percentages significantly deviates from the values measured chemically. Summary of the results of the phase analysis in a table, marking also the modified composition of phases due to isomorphous substitution.

Take part on the demonstration of computer version of the phase analitical method described above (1 hour).

Table 8.2

INTENSITY CONVERSION FACTORS, THEIR STANDARD DEVIATION AND THE RELATIVE INTENSITY CONVERSION FACTORS

Phase name	ICF	St.dev.of ICF	RICF
Hematite	2.6	1	1
Boehmite	1	0.1	1
Cancrinite	1	1	1
Sodalite	1	1	1
Perowskite	1	1	1
Goethite	2.7	0.9	1.2
Corundum	1	1	1
Gibbsite	0.9	0.2	1.2
Diaspore	1	0.2	1
Kaolinite	5.4	1.5	5.4
Portland	1	1	1
Ca-aluminate	1	1	1
Na-titanate	1	1	1
Ilmenite	1	1	1
Siderite	0.3	0.1	0.6
Magnetite	1	1	1
Lithiophillite	4.9	1	4.9
Magnesite	1	1	1
Anatase	0.3	0.1	0.8
Calcite	0.4	0.2	1
Dolomite	0.4	0.2	1
Quartz	0.2	0.1	1
Rutile	0.4	0.1	1
Pyrite	0.6	0.2	1.3
Maghemite	1	1	1
Crandallite	5	2	2

SAMPLE IDENT:						CHART NUMBER:					BAUXITE:		
OXID PHASE	Al_2O_3 %	Fe_2O_3 %	SiO_2 %	TiO_2 %	CaO %	MgO %	S/SO_3 %	P_2O_5 %	Mn_3O_4 %	IGN. L %	INT I.	PHAS %	
BOEH.													
GIBB.													
DIASP.													
KAOL.													
QUARZ													
GOETH.													
HEMA													
ANAT.													
RUTIL													
SIDER													
PYRIT													
CRAND													
CHEM.													

Fig. 8.7

STANDARD FORM FOR BAUXITE PHASE ANALYSIS

3. ELECTRON OPTICAL INVESTIGATIONS

THE MORPHOLOGICAL INVESTIGATION OF ALUMINA HYDRATES AND BAUXITES BY SEM

THE PURPOSES OF THE EXERCISE

SEM is a very useful tool to study the morphological features of bauxites, alumina hydrates and alumina. The purposes of the exercise are the following:

1. Taking of some characteristic photographs about a sandy and a floury type alumina hydrates.

2. Comparison of three selected bauxite samples according to the following points of view:

a) typical grain size
b) space filling
c) morphology of individual crystals contained in the bauxite samples.

3. Evaluation of some pictures of sandy and floury alumina hydrates investigated earlier. Making a table as shown hereunder:

Type of the alumina hydrate: sandy

Largest size of agglomerates: about 160 /um
Smallest size of agglomerates: about 20 /um
Smallest size of individual crystals: about 1 /um.
Characteristic features of single crystals: some wavelike crystal faces, step-like growing faces.
(Comments: these features can be: smooth or wavelike crystal faces, etched pits, growing defects, secondary crystals, twins, layered growing crystals).

SHORT DESCRIPTION OF THE SEM TO BE USED IN THE EXERCISE

Our SEM is a JEOL JSM-U3 type with about 20 nm resolution power in secondary electron mode. The most important parts of the instrument are the following:

1. Body of the microscope: contains an electron gun with a directly heated hairpin-like volfram filament and a Wehnelt cup with an anode; two condenser lenses with two condenser apertures to demagnify the image of the filament; an objective lens with an objective aperture to focus the beam onto the surface of the specimen; coils to scan by the finely focused electron beam on the surface of the specimen; a detector for secondary electrons: this is a photomultiplier with a collector plate; a detector for collecting X-rays generated by the high-energy incident electrons and a specimen holder with a goniometer which can be operated from outside of the column.

2. Evacuation system: it is connected to the body of the microscope. This system contains highly efficient oil--diffusion and rotary pumps to get and maintain about 5×10^{-5} torr (6.65×10^{3} Pa) vacuum inside the column.

3. Power supply and electronic units: by means of these units the microscope can be supplied with the appropriate accelerating voltage (from 5 kV upto 50 kV) and the currents of the lenses can be set, further the brightness and the contrast of the two cathode-ray tubes can be controlled.

SHORT DESCRIPTION OF THE JEE-4B/4C VACUUM EVAPORATOR

This instrument has been designed for the preparation of specimens to be observed by electron microscopes, especially SEM-s. The most important parts of the instrument are the following:

1. Bell jar: it is furnished with two independent electrode-pairs for evaporation of two different kinds of metals or a metal and carbon. There is a cartridge for eighteen specimens of 12 mm diameter. This specimen holder can be tilted and rotated to evaporate the materials uniformly onto all the specimens.

2. Vacuum system: contains a highly efficient oil--diffusion pump and a rotary pump to get and keep the vacuum at about 1×10^{-5}torr (1.33×10^{-3}Pa). There are valves which must be operated manually, therefore the operator must take care to follow the operating sequence.

3. Power supply unit and vacuum meters: there is a torroid transformer to heat up for example the volfram basket for evaporation of gold or copper. If the vacuum in the bell jar is higher than 10^{-2} torr (1.33Pa) it can be measured by an ionization type vacuum meter. Below this pressure a glow discharge tube can be applied.

THE OPERATING SEQUENCE OF THE SEM EXERCISE

1. Preparation of alumina hydrates and bauxites:

Take copper sample holders and paint them with a small quantity of "carbon black" to make good contact between the holder and the sample. By means of tweezers spread small quantity from the alumina hydrate taking care to cover the holder uniformly. In case of a bauxite sample first take a piece of appropriate size and put it on the sample holder (painted by carbon black) with the freshly broken surface outwards. Put the samples into the bell jar of the evaporation instrument, put the sharpened carbon rods on their place between two electrodes, then a gold wire of a few mm length into the W basket. Close the bell jar and evacuate the system to about 1.33 x 10^{-3}Pa. First evaporate carbon with 40 to 50 A, afterward gold by about 30 A (in this latter evaporation take care to the slow increase of the heating current upto the required value; otherwise gold can splash from the basket).

2. Examination of the samples by the SEM:

Put the hydrate specimen into the specimen holder of the JSM-U3. Set the accelerating voltage to 25 kV, the switch of PMT to "5" and the emission current to about 10^{-10}A. First examine the specimen on the TV screen looking for the characteristic shapes of the agglomerates and individual crystals. Then decrease the sample current to about 10^{-11} to 10^{-12}A by setting the condenser lens-switch to a larger value, then take photographs of the characteristic grains, individual crystals and defects taking care to the brightness and the contrast of the pictures. In order to take pictures put the scanning time to 50 sec, the blende of the camera to 5.6. Use Orwo 20 type black and white film to take pictures. In order to study the grain-size distribution of the hydrate sample, take pictures with 100x magnification; i.e. from about 1 μm^2 area. For examining of the space filling of the hydrate-agglomerates, take photographs with 1,000x or 300x magnification depending on the sizes of the agglomerates. In order to study fine structure of the surfaces of individual hydrate crystals, take pictures with 10,000x or 30,000x magnification.

In case of bauxite samples the best method is to make series of pictures taken with different magnifications about some characteristic features.

Summary of the exercise (handing in measurements in the prescribed form)

At the end of the exercise a short report has to be written about the characteristic features (see the starting par of this exercise) of the two different types of alumina hydrates in the form of a table and about the typical morphological details of the selected bauxites.

ENERGY DISPERSIVE ANALYSIS OF BAUXITE SAMPLES

THE PURPOSES OF THE EXERCISE

The energy dispersive spectrometer measures X-ray energy directly producing a spectrum of counts versus energy. The X-rays are excited by the interaction of incident high-energy electrons with the sample.

The purposes of the execise are the following:

1. prepare bauxite specimens suitable for ED analysis;
2. qualitative determination of the elements present in one selected bauxite sample by making ED analysis first on a larger area, after in some "points";
3. making maps of one selected element (for example Fe) about a few parts of the selected bauxite. Comparison to the morphological features.

SHORT DESCRIPTION OF THE INSTRUMENT TO BE USED IN THE EXERCISE

The most important parts of our energy dispersive micro-analyzer produced by EDAX (model 711) are the following:

1. Silicon detector: this is operated at liquid nitrogen temperatures to reduce the dark current and thermal noise and permit the accurate measurement of the very low currents caused by X-rays. The charge collected by the detector is very small since only a few hundred or thousand electrons are produced by each X-ray. It is amplified and filtered. Integration of the signal is used to produce a train of pulses. Each pulse lasts several microseconds, to average out electronic noise and allow precise measurement of its height which is proportional to the energy of the X-ray that produced it.

2. Multichannel pulse-height analyzer: is a special purpose computer which is used to measure and store the above mentioned pulses in a spectrum. Our multichannel analyzer has 800 channels which are divided into two memories of the unit. The analyzer is connected to a DISPLAY to show the spectrum (like as shown in Fig. 8.8). The analyzer is attached to an X-Y recorder (PM 8141) to record the spectra.

3. Nova-3 computer: is applied to carry out e.g. the substraction of the background, stripping of the elements, calculation of the intensity of the elements, quantitative analysis making corrections for the atomic number, absorption and fluorescence effects etc. The computer is connected to a dual floppy-disc system.

THE SEQUENCE OF THE EXERCISE

1. Preparation of the sample:

Embedding: for cold mounting an epoxy type resin is used. The two components are mixed then filled around the sample being in the aluminium ring.

Grinding and polishing: the procedure is long and tedious and extreme care must be taken during the later stages since it is very important to produce flat, smooth surfaces. Three steps have to be applied: course grinding with an alumina suspension type C (grain size: 1 μm), then with another suspension type A (grain size: 0.3 μm), at last with magnesia suspension No. 40-6440-018 produced by Buehler.

Evaporation of gold onto the surface of the specimen: see previous exercise.

2. Examination of bauxite sample by ED microanalyzer:

Switch on the multichannel analyzer and computer and put the two floppy discs into the diskette drive unit. Place your specimen into the sample holder of the JSM-U3 SEM. Set the accelerating voltage to 25 kV, the emission current

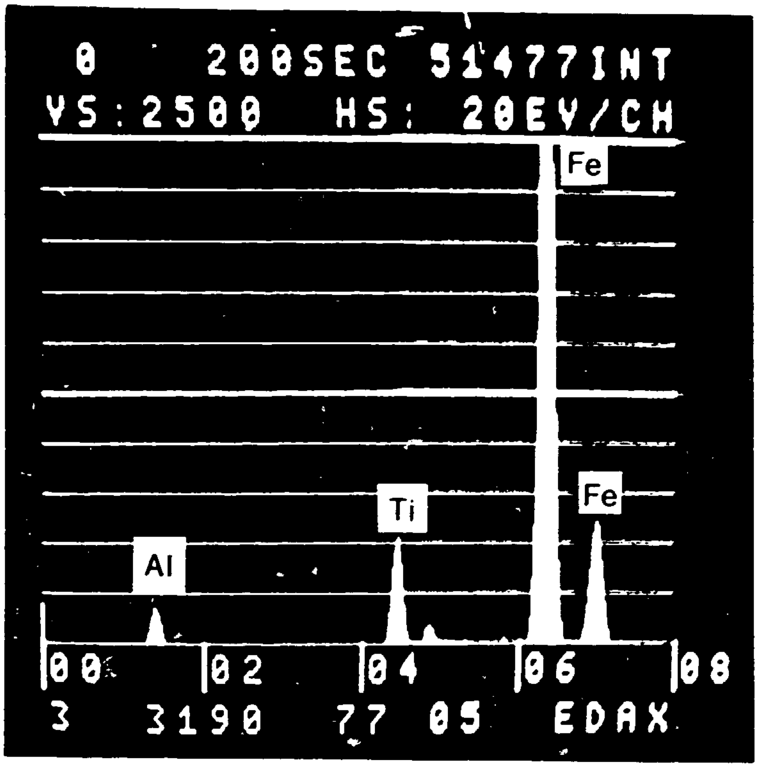


Fig.8.8

THE ENERGY DISPERSIVE SPECTRUM OF A SELECTED AREA FROM A BAUXITE ORIGINATED FROM GHANA to about 1 x 10^{-10}A. First examine the sample on the TV screen looking for the characteristic features of the bauxite. Check the counting rate, choose 100 sec time for analysis and the energy-range from OKeV upto 16KeV and start with the analysis about a characteristic area of the specimen. During analysis use the "Sample Ident." push-button for identification. Load the operating system (DOS 32) using any of the EDAX-supplied masters. When the analysis is ready, use the following program commands: A1 (ENTER from analyzer), B1 (STORE spectrum on diskette) and A4 (STRIP element) in order to get the net peak area for the selected element. Choose a single crystal situated in the selected area and analyse by a "point". To do this switch on the scanning mode switch to point and compare the recorded spectra to the earlier. Make some similar analysis about some selected areas and "points" and compare the elemental compositions.

In order to make map of an element set the "Sample Ident." push-button to the required element and choose an appropriate window for the element. Set the scanning time to 50 or 100 sec put the wire of the 352 Ratemeter to the plug J11 and take out the wire of the photomultiplier from the plug J9. Make pictures from a few selected element--distributions and compare them to the morphological features of the bauxite.

Summary of the exercise (handing in measurement in the prescribed form)

At the end of the exercise a short report has to written about the comparison between morphological features and elemental distributions. The report has to contain the photos of the morphological features, the results of element stripping programs and maps of the selected element distributions.

4. INFRARED AND THERMOGRAVIMETRIC INVESTIGATION

INFRARED SPECTROPHOTOMETRIC INVESTIGATION OF BAUXITE AND RED MUD SAMPLES

PURPOSES OF THE EXCERCISE

As mentioned in Volume 4., infrared spectrophotometry is a useful method to study the main minerals of different types of bauxites, on the basis of vibrational and rotational states of the molecules.

The purposes of the infrared spectrophotometric exercise are the following:

1. Qualitative and quantitative determination of boehmite, gibbsite and kaolinite in case of a Hungarian bauxite sample, by means of a ready calibration curve.
2. To get acquainted with the possibilities of the infrared spectrometric method for investigation of the main phases of the red mud obtained from the examined bauxite.

INSTRUMENT TO BE USED IN THE EXERCISE

The instrument to be used in the exercise is a double-beam, perfectly automatized, UR 20 /produced by Zeiss, Jena/ infrared spectrophotometer. It is working in the analitical wave-number-range: 400-5,000 cm^{-1}. Basic parts of the spectrophotometer are:

1. Source of radiation is made of a 6-8 mm diameter silicon carbide rod. Because of strong emission of the radiation source, water-cooled jacket is applied.
2. Monochromator: there are three prisms in the monochromator permitting spectral resolution. The prisms must be made of materials admitting infrared radiation in the given range and the dependence of their refractive indices on the frequencies should be adequate. According

to these two requirements different prisms must be used in different ranges of spectra. In case of our instrument, KBr /400-850 cm^{-1}/, NaCl /700-4,000 cm^{-1}/ and LiF /1,600-5,000 cm^{-1}/ prisms are applied. Because of the hygroscopic nature of alkaline halides, the monochromator is climatized to 35 °C and dried silica gel is used for the protection of prisms.

3. Detector is a thermocouple.
4. Recorder: the registration takes place on a paper coated by wax. The wave-number absorbance scale is plotted simultaneously with the spectra.

THE SEQUENCE OF MEASUREMENT

To carry out infrared spectrophotometric measurement first we have to make the samples suitable for the investigation. Our samples are pellets and spectroscopically pure KBr produced by Merck can be applied to make pellets. KBr must be dried for 4-5 hours at about 110 °C before using. KBr to be applied in the exercise will previously be dried (i.e. the participants get dried KBr). The bauxite has to be dried also at about 110 °C, then to be cooled in a dessicator. 1.00 gr dried KBr is weighed in an analytic balance and 1.5 mgr from bauxite to be examined has to be weighed and added to KBr. The participants get dried and weighed bauxite and they have to homogenize it in an agate mortar. The homogenized KBr-bauxite mixture is placed into the mould assembled in the exercise and pellets have to be made by means of an air-hydraulic press at 150 kp/cm^2.

After the sample preparation we switch on the spectrophotometer by the main switch, then we set the following parameters:

slit program:	4
aperture:	8
registration rate:	64 cm^{-1}/min
registration paper rate	10 mm/100 cm^{-1}
running-up time of the pen:	16 sec/0-100 %/.

The next step is to put the pellet with bauxite into the "sample beam" and the KBr pellet without bauxite into the "reference beam", respectively. Then the measurement is started by switching the spectrometer knob on. If we also turn on the "end of the program" knob, the instrument will indicate the end of the measurement by sound of bell. During measurement records the IR spectra automatically on the paper covered by wax. The ready spectra can immediately be evaluated.

QUALITATIVE AND QUANTITATIVE EVALUATION OF IR SPECTRA

Among the bauxite minerals boehmite, gibbsite, diaspore, kaolinite and goethite can easily be investigated by IR spectrophotometry. The possiblity of IR spectrometric determination of the other accompanying minerals /for example: calcite, dolomite, pirite, hematite/ is precluded due to different reasons. These reasons can be: absorption band of some minerals is not intensive enough or their small intesity bands are disturbed by the more intensive bands of other phases.

In our domestic samples diaspore can not - or only in a very small quantity - be found, therefore, the characteristic IR absorption bands of boehmite, gibbsite, kaolinite and goethite can be studied. The characteristic frequencies of frequently encountered bauxite minerals are the following:

boehmite: 750, 1080, 1155, 3100, 3290 cm^{-1};
gibbsite: 755, 800, 840, 975, 1030, 3455, 3540, 3625 cm^{-1};
kaolinite: 750, 790, 918, 940, 1015, 1039, 1110, 3628, 3658, 3700 cm^{-1};
goethite: 800, 897, 3130 cm^{-1}.

It can be seen from these data that there are overlapping absorption bands, therefore, the spectra can be evaluated by some difficulties. According to this it is useful to make identification of the phases by means of the vibrational bands of O-H groups.

In IR spectra of red mud samples the most important absorption /extinction/ bands are the following:

sodalite: 460, 560, 625, 680, 740 cm^{-1};
cancrinite: 460, 625, 680, 990 cm^{-1};
goethite: 800, 900 cm^{-1};
boehmite: 1080, 3100, 3290 cm^{-1};
carbonates: 1475 cm^{-1}.

In this case the evaluation is also difficult according to the overlapping bands of some phases. However, the identification of goethite by means of its absorption band at 800 cm^{-1} can be more easily carried out in case of red mud than in case of bauxite. From the spectra of red mud it can be seen /checked/ whether some boehmite remained undigested in the sample. Carbonates can well be identified by their band at 1475 cm^{-1}. In order to determine a given phase quantitatively, a band of the phase must be chosen which is not disturbed by the other bands of different phases. Such specific analytical bands can be the following:

in case of boehmite: 3100 cm^{-1};
in case of gibbsite: 3455 and 3530 cm^{-1};
in case of kaolinite: 3700 cm^{-1}.

The most intensive bands of goethite have small intensities at 800 and 900 cm^{-1}, respectively, and the band at 900 cm^{-1} is highly disturbed by some other aluminium-minerals. In a red mud where these disturbing phases are not present goethite can well be identified.

In order to make quantitative analysis in IR spectra absorbances ($A=\lg I_0/I$) /it was known as extinction in the earlier literature/ of the characteristic analytic bands at the maximums of the bands can be determined using some correction curves.

Evaluating bauxite or red mud samples with known composition-calibration curves can be obtained by plotting the absorbance measure at individual absorption band of the given phase versus the weight per cent of this phase. By means of calibration curves the quantities of boehmite, gibbsite, kaolinite /in case of bauxite/, and goethite /in case of red mud/ can be calculated from the absorbances evaluated in accordance with the IR spectra of the samples. It must be noted that any calibration curve can be applied only for sample with a microstructure similar to the structure of the sample from which the calibration curve was obtained. It is useful to make calibration curves for each bauxite deposit or alumina samples of the plant produced by a given technology.

Summary of the exercise /handing in measurements in the prescribed form/.

At the end of the exercise the short report must contain one recorded spectrum about the selected bauxite sample and the qualitative and quantitative determination of the above mentioned phases of the chosen bauxite in form of a table as shown in Table 8.3.

Table 8.3

Accurate wave-numbers of maximums in the absorption bands detected on the spectrum

1. λ^{-1} /cm^{-1}/
2.
3.

.

.

.

The following phases are present according to the detected absorption band-maxima

mineral	wave-number of the stretching band for unambiguos identification
----	....
....	....

Absorbances of the phases which can be determined quantitatively measured at the analytic band-maxima and elemental concentrations calculated by means of the absorbances and calibration curves

---

phase:

wave-number of the analytic band:

I_o:

I :

lg I_o/I:

concentration
/weight per cent/

DERIVATOGRAPHIC DETERMINATION OF MINERAL COMPOSITION OF BAUXITE AND RED MUD SAMPLES

THE PURPOSES OF THE EXERCISE

The aim of derivatographic measurements of bauxite and red mus samples is to get information about their mineral composition in order to complete the data obtained by other methods. According to the above mentioned aim, the purposes of the exercise are the following:

1. making the derivatogram of one selected bauxite sample;
2. quantitative determination of mineral composition of one bauxite sample originating from Jamaica by means of data obtained from earlier performed wet chemical analysis, derivatographic and X-ray diffractometric measurements.

SHORT DESCRIPTION OF THE INSTRUMENT TO BE USED IN THE EXERCISE

Our derivatograph, as mentioned in Volume 4., is working according to a method developed by L. Erdey - F. Paulik and J. Paulik and was produced by the Hungarian Optical Works. The most important parts of the instrument are:

1. Motor case: this contains one EMG 2895 type A.C. voltage stabilizer and one torroid transformer to set the heating rate to 5 °C/min, 10 °C/min or 20 °C/min.
2. Heating furnaces: the sample can be heated upto 1000 °C or 1500 °C, respectively. The special sample holder crucible is placed on a porcelain tube. The thermocouple introduced through the hole of the porcelain tube has its junction in the infolding bottom of the crucible. This thermocouple is connected in series with opposite polarity with another thermocouple - the latter being

inserted into the centre of a second crucible filled with an inert material - Al_2O_3 annealed at 1300 °C in our case.

3. Balance case: this is attached to the porcelain tube into which the crucible containing the sample is placed. This tube is connected to the analytic balance for weighing the sample. In this case there are three high sensitivity galvanometers: one for measuring the temperature of the sample, the other for establishing the temperature difference between the materials contained in the two crucibles, the third for measuring the rate of weight loss. One set of weights decreasing the sensitivity is placed into this case, too. When the weight changes occurs, a permanent magnet moves freely inside a solenoid.
4. TG signal converter: here any deflection of the balance is converted to an electrical pulse.
5. Lamps case: an approximately homogeneous light emitted by a halogen lamp with high radiated power is distributed to the mirrors of the galvanometers by means of optical fibers.
6. Recorder: has four channal, each of them is connected to one galvanometer. The light signals of the high-sensitivity galvanometers are converted to electronic pulses and amplified by an electronic amplifier. These amplified pulses are registered by an alternatively moving recording pen. Four curves /T, DTA, TG and DTG/ are recorded on a registration paper placed on a drum.

THE SEQUENCE OF DERIVATOGRAPHIC MEASUREMENT

The instrument is switched on by the main switch. The heating rate is chosen normally to 10 °C/min. The motor is set to 100' and the starting voltage to 77 V, respectively. (This value was determined by calibration measurements carried out earlier.) The TG-signal converter and the halogen lamp we are switched on and the galvanometers of the registration unit are set free. The sensitivity of the galvanometers is set according to the sample. To study bauxites for DTA: 1/10 mV, for DTG: 1/15 mV, for T: 1000 °C can be set. At the registration unit the sign "T" is put to 20 °C. TG signal is set in accordance with the "0" position of the balance.

Weighing the sample is carried out in the balance case similarly to other analytic balances. Depending on the quality of bauxite the weighing is performed to the special platinum crucible with knowledge of ignition loss. If the bauxite contains a lot of boehmite, lgr bauxite is weighed, if it has a great quantity of gibbsite, less is weighed than in the earlier case: about 0.8 gr. In this latter case the offset of the balance is set to 200 mgr.

The averaged bauxite milled below 63 μm is put into the crucible by a spatula. After carrying out the weighing, furnaces are fixed to the crucibles. The balance is set free and it is necessary to wait for its neutral position, afterward the DTG switch is set free. Light signals have to be checked and motors of recording apparatus and writing heads have to be switched on. Heating unit and the motor of program-disc are switched on. The derivatogram is ready in 100 min, since the temperature reaches 1000 °C by this time. Then the instrument is switched off, DTG switch is set off, afterwards the balance is arrested. The furnace has to be lifted up a little. The derivatogram can be evaluated immediately.

EVALUATION OF DERIVATOGRAMS

Evaluation is carried out by a so-called complex method. This means that wet chemical analysis and X-ray diffractometric data are necessary to the evaluation of the curves of thermal analysis.

Temperature-values can be marked by a ruler on the T curve. The temperatures of endothermic or exothermic peaks in DTA and DTG curves, respectively, can be read off. Knowing these peak-temperatures a qualitative determination of individual components can be obtained; these data can be compared with the data of X-ray diffractograms (see Table 8.4).

The quantitative analysis can be carried out by means of TG and DTG curves. The starting and ending points of individual reactions are marked on DTG curve, then these are projected onto the TG curve. The loss of weight /in mg/ of each component can be read off the TG curve. Knowing the stoichiometric formula and the weighing, the percentual quantity of each component can be obtained. For example in case of gibbsite:

$$2Al/OH/_3 = Al_2O_3 + \underline{3H_2O}$$

in case of boehmite:

$$2AlO/OH/ = Al_2O_3 + \underline{H_2O}$$

in case of goethite:

$$2FeO/OH/ = Fe_2O_3 + \underline{H_2O}$$

and in case of kaolinite:

$$Al_2O_3.2SiO_2.2H_2O = Al_2O_3 + 2SiO_2 + \underline{2H_2O}$$

Derivatographic Determination of the Mineral Phases Occurring Most Frequently in Bauxites and Red Muds

Table 8.4

Mineral	Formula	Component lost	Peak temperature °C	Temperature range °C	Calculation formula
Gibbsite	$Al_2O_3.3H_2O$	$3H_2O$			
		$2.75H_2O$	320-340	260-380	Al_2O_3 % = 101.94.G/49.555
		$0.25H_2O$	540-560	500-600	Gibbsite % = 156.0.G/49.555
Boehmite (Diaspore)	$Al_2O_3.H_2O$	H_2O	540-560	440-600	Al_2O_3 % = 101.94.G/15.02 Boehmite % = 119.96.G/18.02
Kaolinite	$Al_2O_3.2SiO_2.2H_2O$	$2H_2O$	590-610	560-700	Al_2O_2 % = 101.94.G/36.03 SiO_2 % = 120.12.G/36.04 Kaolinite % = 258.10.G/36.04
Goethite	$Fe_2O_3.H_2O$	H_2O	360-380	340-420	Fe_2O_3 % = 159.70.G/18.02 Goethite % = 177.72.G/18.02
Calcite	$CaCO_3$	CO_2	760-780	680-820	CaO % = 56.03.G/44.01 Calcite % = 100.09.G/44.01
Dolomite	$CaMg(CO_3)_2$	$2CO_2$	800-820 960-980	520-920	CaOMgO % = 96.40.G/88.02 Dolomite % = 184.42.G/88.02
Sodalite	$1.2Na_2O.Al_2O_3.1.7SiO_2.1.7H_2O$	$1.7H_2O$	-	100-400	Al_2O_3 % = 101.94.G/30.63 Na_2O % = 80.58.G/30.63 SiO_2 % = 102.10.G/30.63 Sodalite % = 315.25.G/30.63
Ca-Al-silicate-hydrate	$2CaO.Al_2O_3.2SiO_2.4H_2O$	$4H_2O$	360-380	280-440	CaO % = 168.24.G/72.08 Al_2O_3 % = 101.94.G/72.08 SiO_2 % = 120.12.G/72.08 Ca-Al-sil.-hydr. % = 462.38.G/82.08
Ca-Al-silicate-hydrate	$3CaO.Al_2O_3.2SiO_2.2H_2O$	$2H_2O$	360-380	280-440	CaO % = 168.24.G/36.04 Al_2O_3 % = 101.94.G/36.04 SiO_2 % = 120.12.G/36.04 Ca-Al-silicate-hydrate % = 426.34.G/36.04
Calcium hydroxide	$Ca(OH)_2$	H_2O	520	470-550	CaO % = 50.08.G/18.02 $Ca(OH)_2$ % = 74.10.G/18.02
Calcium aluminate	$3CaO.Al_2O_3.6H_2O$	$4H_2O$	350	280-420	CaO % = 168.24.G/72.08 Al_2O_3 % = 101.94.G/72.08 Calcium aluminate hydrate % = 378.30.G/72.08

G = measured weight change in the given temperature range.

For calculating boehmite the residual 0.25 mole water of gibbsite shall be subtracted from the weight change.

In some special cases the calculation can not be carried out with data according to the stoichiometric composition, and experimental factors must be taken into account. For example gibbsite bleeds 2 1/2 moles of its water content upto 400 °C, the rest is lost at a higher temperature, in the position of the boehmite. Therefore, this value must be substracted from the weight loss of boehmite. In bauxite samples boehmite contains more than one mole water. According to a lot of investigations in the case of bauxite goethite contains 1 1/3 moles of water. Careful calculation is necessary to give the correct composition, comparing it with all the information obtained by other methods.

Summary of the exercise /handing in the measurement in the prescribed form/.

At the end of the exercise a short report has to be written containing one ready derivatogram about the chosen bauxite and a table with the qualitative and quantitative determination of the mineral composition of a selected bauxite examined earlier. The table can be similar to the Table 8.5.

Evaluation of Derivatograms of Bauxite and Red Mud from Halimba

(see Fig. 8.9)

Table 8.

Sample	Temperature range °C	Weight loss %	Mineral comp.	Mineral comp. %	Al_2O_3 %	Na_2O %	SiO_2 %	Fe_2O_3 %	CaO %	Ign. loss %
Bauxite (Halimba)	270-380	5.2	Gibbsite	16.4	10.7	-	-	-	-	
	380-450	1.0	Goethite	9.9	-	-	-	8.9	-	
	450-570	5.54 (6.0-0.46)	Boehmite	37.0	31.4	-	-	-	-	
	570-720	2.1	Kaolinite	15.1	6.0	-	7.0	-	-	
	720-800	0.8	Calcite	1.8	-	-	-	-	1.0	
			Derivatograph.		48.1	-	7.0	8.9	1.0	8.3
			Wet analysis		49.2	-	6.8	23.7	1.1	8.4
Red mud (Halimba)	100-320	4.5	Sodalite	46.3	15.0	11.8	15.0	-	-	
	320-460	1.9	Goethite	18.8	-	-	-	16.9	-	
	460-690	0.9	Boehmite (0.4)+Pyrite	2.4	2.0	-	-	-	-	
	690-820	0.9	Calcite	2.0	-	-	-	-	1.1	
			Derivatograph.		17.0	11.8	15.0	16.9	1.1	8.8
			Wet analysis		16.3	10.8	14.3	44.2	1.5	8.0

Boehmite was calculated by subtracting the 0.25 mole water of gibbsite from the weight loss. The difference between the amounts of Fe_2O_3 determined by wet analysis and Fe_2O_3 determined in form of goethite gives the hematite content of samples. Thus hematite content of bauxite is 23.7 - 8.9 = 14.8 %; hematite content of red mud is 44.2 - 16.9 = 27.3 %.

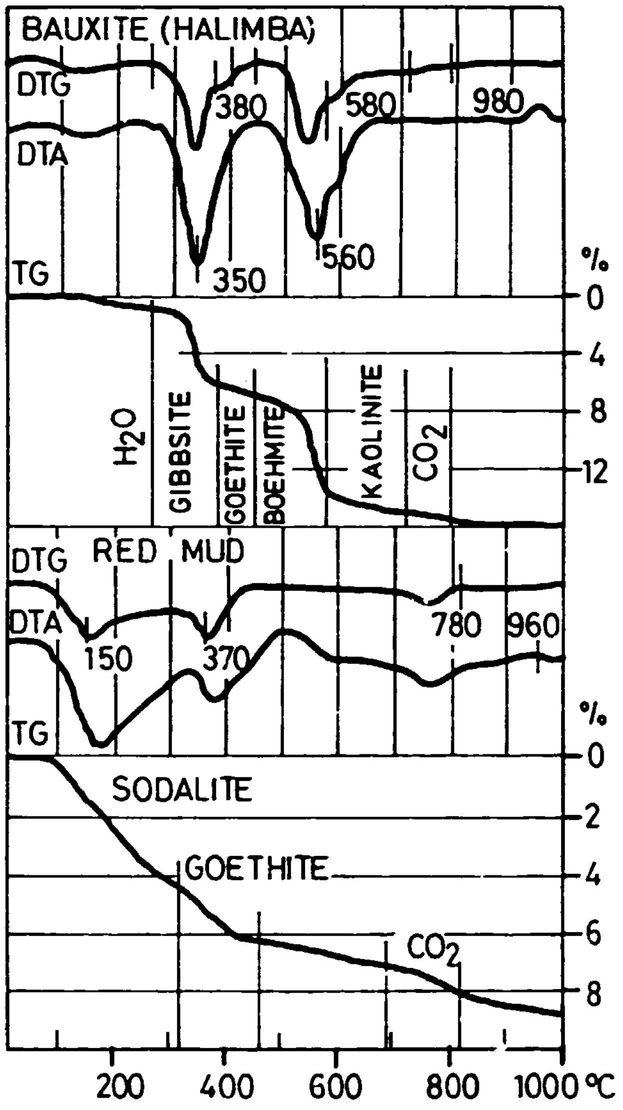


Fig. 8.9

DERIVATOGRAM OF A HALIMBA BAUXITE

5. CHEMICAL ANALYSIS OF BAUXITE (AND RED MUD)

DETERMINATION OF MOISTURE OF AN AIR DRY BAUXITE SAMPLE

Principle: A weighed sample of an air-dry bauxite is heated at 130 °C during three hours. The loss in weight is equal to the hygroscopic water.

Procedure: Place a clean opened weighing bottle in the drying oven and heat it at 130 °C during 30 minutes. Close it in the oven and allow to cool in the desiccator filled with silica-gel. Place the closed bottle beside the balance for 20 minutes, open it for a moment and weigh (T). Transfere 2-3 g of bauxite to the weighing bottle, close it and weigh (B). Dry the sample for three hours at least at 130 °C taking off the cover. Carry the dried sample in the weighing bottle to the desiccator and closed. After cooling period weigh the dried sample likewise mentioned before (C).

Calculations:

$$\text{Moisture (loss in weight) } \% = 100 \cdot \frac{B - C}{B - T}$$

where T the weight of empty weighing bottle (g)
B the weight of bottle and sample before drying (g)
C the weight of bottle and sample after drying (g)

Precision: Variation coefficient is 2 at 1-2 % moisture.

Time consumption: 3 1/2 hours.

DETERMINATION OF LOSS ON IGNITION OF BAUXITE

Principle: A weighed sample of an air dry bauxite is heated at 1100 °C during two hours. The loss in weight is equal to the water and CO_2 content, however, some side--effects have to be considered too originating from the heat reaction of minor components.

Procedure: Ignite a cleaned platinum crucible with cover in an electric furnace at 1100 °C during ten minutes. Cool it in a desiccator and weigh (T). Introduce about 1-2 g of bauxite and weigh (B). Heat slowly the covered crucible to red and hold at this temperature (400-450 °C) for 15 minutes. Ignite the opened crucible with the sample at 1100 °C for two hours. After ignition cover the crucible immediately and place it in to a desiccator. After 20 minutes cooling weigh it (C).

Calculations:

$$\text{Loss on ignition } \% = 100 \cdot \frac{B - (C+H)}{B - (T+H)}$$

where T the weight of empty crucible (g)
B the weight of crucible and sample before ignition (g)
C the weight of crucible and sample after ignition (g)
H moisture content of bauxite sample (g)

Precision: Variation coefficient 0.2.

Time consumption: 2 1/2 hours.

DISSOLUTION OF BAUXITE TO DETERMINE ITS SiO_2, Al_2O_3 AND TiO_2 CONTENT

Principle: A weighed sample of an air dry bauxite is solved in sulfuric acid/hydrogen peroxide mixture. The silica content can be separated as insoluble dehydrated silicic acid.

An alternative dissolution may be performed in triacid mixture ($HCl - HNO_3 - H_2SO_4$).

If bauxite contains Al_2O_3 as diaspore a preliminary transformation is needed by a heat treatment with $Na_2CO_3 - KNO_3$.

Procedure: Weigh 0.9 - 1.1 g sample on analytical balance and transfer it to a 400 ml beaker, swirling it after addition of 10 ml of distilled water. Add 30 ml of 1:1 H_2SO_4 and 5 ml of concentrated H_2O_2 and evaporate till the white fumes of sulfurtrioxide appear. Let the dissolved material cool and dilute carefully with 100 ml distilled water washing the salts from the watch glass to the beaker too. Heat the beaker without boiling till the salts dissolve. (Silicic acid remains as precipitate.) Filtrate the hot mixture on a filter of medium grades of porosity to a 400 ml beaker and wash the silicic acid precipitate with hot diluted (1 %) sulfuric acid six times. The volume of filtrate is about 250-300 ml. Determine the SiO_2 content from the precipitate while evaporating the filtrate to 170-180 ml.

PRELIMINARY TREATMENT OF BAUXIT SAMPLES CONTAINING DIASPORE

Weigh 0.9-1.1 g sample and 0.8 g Na_2CO_3, 0.2 g KNO_3 mix in a platinum crucible. Heat the crucible in an electric furnace at 900 °C for 30 minutes. After cooling transfer the mixture with the help of 10 ml distilled water to a 400 ml beaker and continue the procedure as usually.

DETERMINATION OF SiO_2 CONTENT OF BAUXITE

Principle: The filtrated and washed precipitate (insoluble residue of dissolved bauxite) is ignited at 1000 °C. After cooling the silicic acid is evaporated as H_2SiF_6 with hydrofluoric acid in the presence of sulfuric acid. The residue is ignited again. The loss in weight is equal to the SiO_2 content.

Procedure: Transfer the wet precipitate prepared according to the dissolution procedure to a platinum crucible and dry it on a hot plate or in an owen. Heat it in an electric furnace, keep the door open till the filter paper is ashed and ignite at 1000 °C for one hour. Let the crucible cool in a desiccator and weight it (A). Wet the ignited precipitate with 5-10 drops of 1:1 H_2SO_4 and pour 5-8 ml of concentrated HF solution to the crucible. Evaporate the mixture without boiling to dry. Heat the residue on a gas burner to red and ignite in a furnace at 1000 °C for 20 minutes. After cooling weigh it (B). Fuse the residue with 1 g of $K_2S_2O_7$ for 5-10 minutes at about 400 °C and after cooling solve the mixture with the filtrate of the dissolution process. Pour the solution and the filtrate to a 250 ml volumetric flask, wash in the crucible and beaker too. After cooling fill it to the mark with distilled water. This solution is used to determine the Al_2O_3 and TiO_2 content.

Calculation:

$$SiO_2\ \% = 100 \cdot \frac{A - B}{M - H}$$

where A the weight of crucible and ignited precipitate (g)
B the weight of crucible and ignited residue (g)
M the weight of air-dry bauxite sample (g)
H the moisture of bauxite (g)

Precision: Variation coefficient 1.

Time consumption: 5 hours (with dissolution procedure).

DETERMINATION OF Al_2O_3 CONTENT OF BAUXITE

Principle: The aluminium content of an aliquot of the dissolved bauxite is separated as soluble sodium aluminate from the other components remaining as insoluble hydroxides. The aluminium can be determined by complexometric titration, taking into account the loss due to the adsorption of aluminate on the hydroxide precipitate.

Procedure: Transfer 100 ml of aliquot of the solution of bauxite with a pipet to a 400 ml beaker. Boil the solution and add 25 ml of 10 F NaOH and 5 ml of 3 % hydrogen peroxide with a graduated cylinder and boil it exactly for three minutes. Cool the solution, transfer it to a volumetric flask and filtrate using the filtration apparatus seen on Fig. 8.10. Set the position of the ring on the stand so that the rubber plate fit to the edge of the funnel. Shake the flask containing the solution to be filtrated and place it to the stand, closing the orifice with your finger. Open the flask and loosen the Hoffmann valve. As the filtration starts, the solution fills the funnel to the neck of the upper flask and only the filtered solution will flow from the flask. After quantitative filtration transfer 100 ml of filtrate with pipet to an Erlenmayer flask and pipet 20 ml of 0.12 F EDTA to the solution. After mixing neutralize the solution in the presence of phenolptalein indicator with 1:1 HCl. Add 10 ml of acetate buffer solution of pH 5.5 and

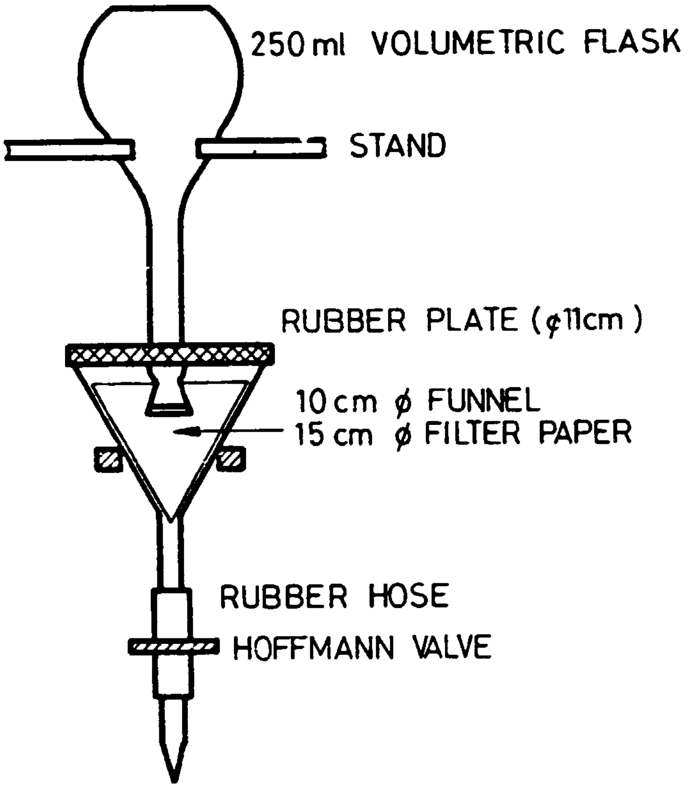


Fig. 8.10
ANALYTICAL FILTER

some boiling stones, cover it with watch glass and boil for 5 minutes. Let the solution cool and titrate with 0.05 F zinc acetate in the presence of 10 drops of 0.1 % xilenolorange to red-violet colour (V ml).

The titer of the EDTA solution must be determined daily as follows. Transfer 100 ml of 1 F NaCl solution and pipet 20 ml of 0.12 F EDTA to an Erlenmayer flask. Add 100 ml of acetate buffer of pH 5.5 and 10 drops xilenolorange indicator to the solution and titrate with zinc acetate titrant (V_o).

Calculation:

$$Al_2O_3\ \% = 100\ .\ \frac{(V_o - V)\ t\ .\ 6{,}25}{M - H}$$

where V_o the consumption of zinc acetate titrant at blank (ml)
V the consumption of zinc acetate titrant at sample (ml)
t the titer of zinc acetate titrant (g/ml)
M the weight of air dry bauxite sample (g)
H the moisture of bauxite (g)

Precision: Variation coefficient is 0.5.

Time consumption: 1 hour.

Note 1.

If the bauxite has a large CaO content a preliminary separation is needed with urotropine.

Not 2.

The loss of Al content due to the adsorption effect of hydroxide must be corrected depending on the Al_2O_3 and Fe_2O_3 content of the sample according to the next table.

Al_2O_3 %	Fe_2O_3 % 15	20	25
45	0.15	0.20	0.25
50	0.15	0.20	0.25
55	0.15	0.20	0.30

The properly selected value must be added to the determined Al_2O_3 content.

DETERMINATION OF TiO_2 CONTENT OF BAUXITE

Principle: The titanium forms peroxo complexes of yellow colour with hydrogene peroxide. The intensity of light is direct proportional to the concentration of the titanium content. Measure the intensity of light with a spectrophotometer. The disturbing effect originated from the yellow colour of the ferric complexes can be eliminated with phosphoric acid.

Procedure: Transfer 50 ml of aliquot of the solution of bauxite to a 100 ml volumetric flask with pipet. Add 5 ml of 10 % hydrogen peroxide and fill to the mark with sulfuric acid - phosphoric acid mixture. Measure the optical density of the solution at wavelength of 410 nm in a cuvet of 1 cm of pathlength. The reference cuvet is filled with distilled water. The exact performance of light intensity measurement is written in the manufactures manual.

Prepare the calibration curve as follows: Transfer 2, 5 and 10 ml of standard solution to three 100 ml volumetric flasks with buret which are equal to 1.0, 2.5 and 5 mg of TiO_2. Pour 40 ml of sulfuric acid - phosphoric acid mixture to the flask with graduated cylinder add 10 ml of 10 % hydrogen perioxide and 4 ml of 1:1 HCl. Fill the flask to the mark with distilled water and shake. Measure the extinction of the solution at wavelength of 410 nm in a cuvet of 1 cm of pathlength. The reference cuvet is filled with distilled water.

Calculation: Read the TiO_2 quantity from the calibration curve (a) corresponding the measured optical density.

$$TiO_2\ \% = 100 \cdot \frac{10 \cdot a}{M - H}$$

where a the TiO_2 content of the part of sample (g)
M the weight of air-dry bauxite sample (g)
H the moisture of bauxite (g)

Precision: Variation coefficient is 5.

Time consumption: 1/2 hour.

DETERMINATION OF TOTAL IRON CONTENT OF BAUXITE

Principle: Fuse the bauxite sample with KOH flux, add sulfuric acid and permanganate to oxidize the iron to ferric. The excess of permanganate is removed with concentrated hydrocloric acid and the ferric ions are reduced with a little excess of $SnCl_2$ to ferrous ions. The ferrous ions are titrated with potassium dichromate titrant in the presence of diphenylaminesulfonic acid after addition of $HgCl_2$ and phosphoric acid.

Procedure: Weigh in 0.5-0.6 g of air-dry bauxite to a dry silver dish. Add 7-8 g of granulated potassium hydroxide and 5 ml of ethylalcohol Burn the alcohol moving the dish, fuse the mixture on a gas burner and heat it for five minutes. Cool the fused material and solve it in 50 ml of distilled water. Pour the solution to a 300 ml Erlenmayer flask with the precipitate solved from the dish with three times 10 ml of 1 F sulfuric acid. Add 15 ml of 1:1 sulfuric acid to the flask. Boil the solution and add 2 % potassium permanganate dropwise till the colour of solution remains violet. Add 15 ml concentrated hydrocloric acid, boil it and add 5 % $SnCl_2$ dropwise until the yellow colour of the digest changes to colorless and add even two drops in excess. Cool immediately to below room temperature pour once 20 ml of 5 % $HgCl_2$ into it and add 20 ml of 20 % phosphoric acid after one minute wait. Start the titration, them add 2-3 drops of 0.2 % diphenylsulfonic acid indicator with 0.05 F $K_2Cr_2O_7$ titrant. The end point colour is violet.

Calculation:

$$Fe_2O_3\ \% = 100 \cdot \frac{V \cdot 0.003992}{M - H}$$

where V consumed $K_2Cr_2O_7$ titrant (ml)
M the weight of air-dry bauxite sample (g)
H the moisture of bauxite (g)

Precision: Variation coefficient is 0.2.

Time consumption: 45 min.

DETERMINATION OF CHROMIUM AND VANADIUM CONTENT OF BAUXITE

PRINCIPLE

After an alkaline oxidation fusion of bauxite the fuse is extracted with hot distilled water. The chromium is in the form of chromate, the vanadium forms vanadate in this solution. The chromium and vanadium content can be measured together with titration performed with Fe^2 titrant, and the end point can be detected potentiometrically with the application of platinum and reference electrode pair. The products of this reduction are V (IV) and Cr (III) ions. After this titration the vanadium can be selectively oxidized with permanganate and the excess of permanganate can be decomposed with sodium azide. The vanadium content can be measured once more with Fe^{2} titrant.

PROCEDURE

Weigh 5 g air-dry bauxite, 30 g of granulated sodium hydroxide and 1 g of sodium peroxide to a silver crucible. Melt this mixture with a Bunsen lamp and keep it in melt phase for half an hour. Let it cool and add about 40 ml of distilled water, boil it, and pour the solution to a 500 ml volumetric flask. Repeat this till the whole melt is solved. Fill up the solution with distilled water to the mark, and let the precipitate settle. Pipet 200 ml from the clear solution to a 400 ml beaker and add 40 ml of 1:1 diluted sulfuric acid.

Take the electrode pair to the solution and titre with 0.01 F ferrous ammonium sulfate. Stir the solution continuously with a magnetic stirer during the titration.

Give 0.1 F of $KMnO_4$ to the solution till its colour remains pink. Add 3 ml of 5 % sodium azide solution and after five minute waiting, titre the solution with ferrous ammonium sulfate likewise before.

Calculation

$$V_2O_5\ \% = 100 \cdot \frac{V_2 \cdot f \cdot 0.000909 \cdot 2.5}{G - H}$$

$$Cr_2O_3\ \% = 100 \cdot \frac{(V_1 - V_2) \cdot f \cdot 0.000253 \cdot 2.5}{G - H}$$

where	V_1	consumed volume of titrant at the first titration (ml)
	V_2	consumed volume of titrant at the second titration (ml)
	f	titer of the ferrous ammonium sulfate titrant
	G	weight of air-dry bauxit sample (g)
	H	moisture content of bauxite (g)

PRECISION

Variation coefficient is 3.

TIME CONSUMPTION

Half an hour.

6. BAUXITE GRINDING AND DIGESTING LIQUOR PREPARATION

BAUXITE GRINDING

The aim of bauxite dressing is to get the ore more premeable and digestable for digesting liquor. However, the excessive comminution spoils the red mud settling and it is detrimental to the energy consumption too. So the optimal grain size after comminution (at minimal energy consumption) is to be guaranted.

A suitable practice, for characterizing the grindability is to determine the Bond index described in the periodical "Zement-Kalk-Gips" No. 10/1957 in details.

Nevertheless, in the practice of manufacturing alumina, wet grinding is carried out in presence of caustic (digesting liquor) when the caustic has also chemical and disintegrative effect on the ore. It is advisable to model this process also in laboratory. This laboratory test serves only for getting acquainted with the method; if someone wants to determine the optimal conditions of grinding (liquor concentration, solid concentration, ball charge in mill, comminution time) he has to carry out a set of test at various, systematically chosen parameters.

AIMS OF THE LABORATORY TEST

1. Getting acquainted with the grinding instruments used for laboratory investigations (jaw crasher, hammer mill, ball mills, colloid mill, dry sieve series, wet sieve series, air jet sieve, air jet classsifier).

2. Carrying out a grinding test on a Hungarian bauxite sample; evaluation of grindability based on bauxite grain size distribution determined before and after grinding.

EXECUTION OF TEST

a) Prepare a slurry of 150 gs dry bauxite - grain size less than 3 mm - and 450 mls distilled water and feed to the wet sieve series gradually. Weight the weight of each screen oversize fraction after 3 hours drying on 105 °C for the initial grain size distribution determination.

b) Carry out the wet grinding in a porcelain ball mill. The sizes and ball charge of the mill is fixed. The pulping liquor composition and quantity depends on the quality of the examined bauxite.

Using this Hungarian Iszkaszentgyörgy bauxite prepare the slurry from 150 gs of dry bauxite sample and 500 mls of Almásfüzitő plant liquor (caust. Na_2O = 200 gpl, caust. molar ratio = 3.5) and feed the slurry into the ball mill. Stop rotating the mill after 0.5 hour grinding, remove the slurry from the balls and centrifuge it. Repulp the solid phase with 500 mls boiling water for removing its caustic content and centrifugate the slurry again. Repeat it 3 times.

c) Repulp the residual solid material with 450 mls of distilled water and feed it gradually to the wet sieve series, and determine the grain size distribution of bauxite after grinding as it is written in paragraph a).

d) Plot the screen oversize fraction curves (before and after grinding). Evaluate the effectivity of grinding by making a comparison between the two curves.

DIGESTING LIQUOR PREPARATION

Depending on the technological investigations connected to the bauxite evaluation, plant liquors contaminated with organic and inorganic inpurities of synthetic sodium-aluminate liquors are applied to laboratory investigations.

For most of the technological investigations (grinding, predesilication, digestion, red mud settling, precipitation) a plant liquor used for processing similar bauxite to the investigated one is applied. So, the laboratory investigations approach much more the plant conditions, because the organic and inorganic contaminants of the solution have significant influence on the technological processes like on the Al_2O_3 dissolution and equilibrium solubility in digestion, $Al(OH)_3$ yield and product alumina hydrate quality in precipitation etc. (see Vol.2.).

Contaminant-free synthetic liquor is used in cases when the aim is to examine the dissolution and accumulation of some contaminants (e.g. organic content), or the technological effect of certain contaminants is studied.

PREPARATION OF SOLUTIONS OF GIVEN CONCENTRATION AND MOLAR RATIO

Using Plant Sodium-aluminate Liquor

The required molar ratio is fixed by dissolving NaOH or $Al(OH)_3$ (at 140-150 ^{o}C). The appropriate concentration is fixed by dilution in case of using plant liquor of known concentration and molar ratio. The required salt level of the liquor can be adjusted by salt removal with evaporation or Na_2CO_3 addition if necessary.

Synthetic Solution

Dissolve the required amount of NaOH in water to fix the caustic concentration and add in small quantities the required amount of chipped aluminium of appropriate purity to fix the given molar ratio. Carry out this process in a room fire apart, under hood because hydrogen is escaping at dissolution by the following form:

$$Al + NaOH + 3H_2O = Na\left[Al(OH)_4\right] + 1\,{}^1/_2\ H_2\uparrow$$

The solution warms up and evaporates at dissolving, hence, the volume of the solution is to be fixed after dissolving and cooling to the room temperature.

EXERCISE

Prepare digestion liquor solution for digestion experiments of concentration and molar ratio fixed by the instructor.

Caution: Use protecting gloves and mask if you handle strong caustic every case!

7. PREDESILICATION OF BAUXITE

INTRODUCTION

Predesilication of bauxites means the dissolution of reactive SiO_2 content of bauxites into sodium-aluminium-hydro silicates. The principal aim of predesilication is to reduce the scaling formation rate at the slurry side of the indirectly heated equipment of alumina production (slurry preheaters, autoclaves), bringing about an increase in the operation cycle time and a decrease in the amount of the specific energy requirement for heating. Similarly, a significant objective is to ensure low SiO_2 content of alumina - principally in case of processing gibbsitic bauxites.

Parameters of the Predesilication Process:

Temperature: 95-100 °C
Retention time: 4- 8 hours
Solids content: 200-600 g/l
Aluminate liquor concentration
in terms of kNa_2O: 130-180 g/l

In case of using the above parameters, the reactive silica content can be transformed into sodium-aluminium-hydrosilicate with 60-80 per cent efficiency, in the function of the reaction characteristics of the bauxites' SiO_2 content. Determination of the predesilication efficiency is based on determining the increasing Na_2O content of the solid phase, simultaneously with the progression of the predesilication process (sodalite formation).

The predesilication efficiency can be calculated by the following formula:

$$\eta_{SiO_2} = \left(1 - \frac{Na_2O_m \cdot Fe_2O_{3\,bx}}{Fe_2O_{3\,m} \cdot SiO_{2\,r} \cdot 0.688}\right) \cdot 100 \quad \text{per cent,}$$

where:

Na_2O_m : Na_2O content in the predesilicated bauxite (slurry)

$Fe_2O_{3\ m}$: Fe_2O_3 content in the predesilicated bauxite (slurry)

$Fe_2O_{3\ bx}$: Fe_2O_3 content of the bauxite to be processed

$SiO_{2\ r}$: reactive SiO_2 content in the bauxite to be processed

0.688 : weight ratio of Na_2O- and SiO_2 content in the sodium-aluminium-hydrosilicate

EQUIPMENT AND MATERIALS REQUIRED FOR THE EXPERIMENTS

- oil bath autoclave of 6 bombs, which can be thermostated by ± 1 °C accuracy. Detailed description of the equipment is given in the chapter on digestibility tests (8 experiments)
- bauxite of known chemical- and mineral composition, ground for 0.1-0.5 µm grain size
- sodium-aluminate solution of known composition ($Na_2O_{caust.}$; Al_2O_3; M; SiO_2)
- hot wash liquor of 2 g/l $Na_2O_{caust.}$ content
- laboratory centrifuge (revolution number: 3000 r/min.)

PERFORMING OF THE EXPERIMENT

The amount of bauxite necessary to attain the given solids content, and 150 ml digestion liquor are weighed in the digestion bombs. After sealing the bombs, they are placed into the oil bath preheated to 95 °C, when the temperature falls slightly. The experiment is considered to be started after the required temperature is attained.

During the experiment, samples are taken for 0.5; 1.0; 1.5; 2.0; 4,0 and 8.0 hours after the starting time.

Liquid and solid phases of the samples are separated by centrifuge.

The following components of the liquid phase must be determined:

$Na_2O_{caust.}$ content
Al_2O_3 content
Molar ratio
SiO_2 content

Predesilicated bauxite has to be prepared for the solid phase analysis, requiring the following measures:

- washing of the mud - by the use of 300 ml washing liquor of 95 °C temperature, 2 g/l Na_2O content - three times per each sample
- mud drying - on 110 °C, for 12 hours
- mud grinding - to below 0.1 or 0.063 µm, resp.

The following components of the desilicated mud must be determined: Loss on Ignition; Fe_2O_3; SiO_2; Na_2O.

EVALUATION OF THE EXPERIMENT RESULTS

Progression of the predesilication process has to be followed in the function of time, both from the solid- and liquid phases' aspect.

Recording of the experiment conditions, measured and calculated data required for the evaluation, and the diagram illustrating the result is shown by the example of Tables 8.6 and 8.7 and Fig.8.11.

Table 8.6

Bauxite:

	%
L.O.I.	
Fe_2O_3	
SiO_2 total	
SiO_2 reactive	

Aluminate liquor:

	g/l
$Na_2O_{caust.}$	
Al_2O_3	
Molar ratio	
SiO_2	

Table 8.7

No. of Sample	Bauxite slurry content g/l	Tempera-ture ^{o}C	Time h	Composition of liquid phase				
				$Na_2O_{caust.}$ g/l	Al_2O_3 g/l	Molar ratio	SiO_2 g/l	$\frac{SiO_2}{Na_2O_{caust.}} \cdot 10^2$
1.								
2.								
3.								
4.								
5.								
6.								

Composition of predesilicated bauxite

No.of Sample	Loss on ignigion %	Fe_2O_3 %	SiO_2 %	Na_2O %	R_1 kg/kg	R_2 kg/kg	$\eta\ SiO_2$ %
1.							
2.							
3.							
4.							
5.							
6.							

$$R_1 : \frac{Na_2O}{Fe_2O_3} = \quad R_2 : \frac{SiO_{2\ r} \cdot 0.688}{Fe_2O_{3\ bx.}} =$$

$$\eta\ SiO_2\ \%: \left(1 - \frac{R_1}{R_2}\right) 100 =$$

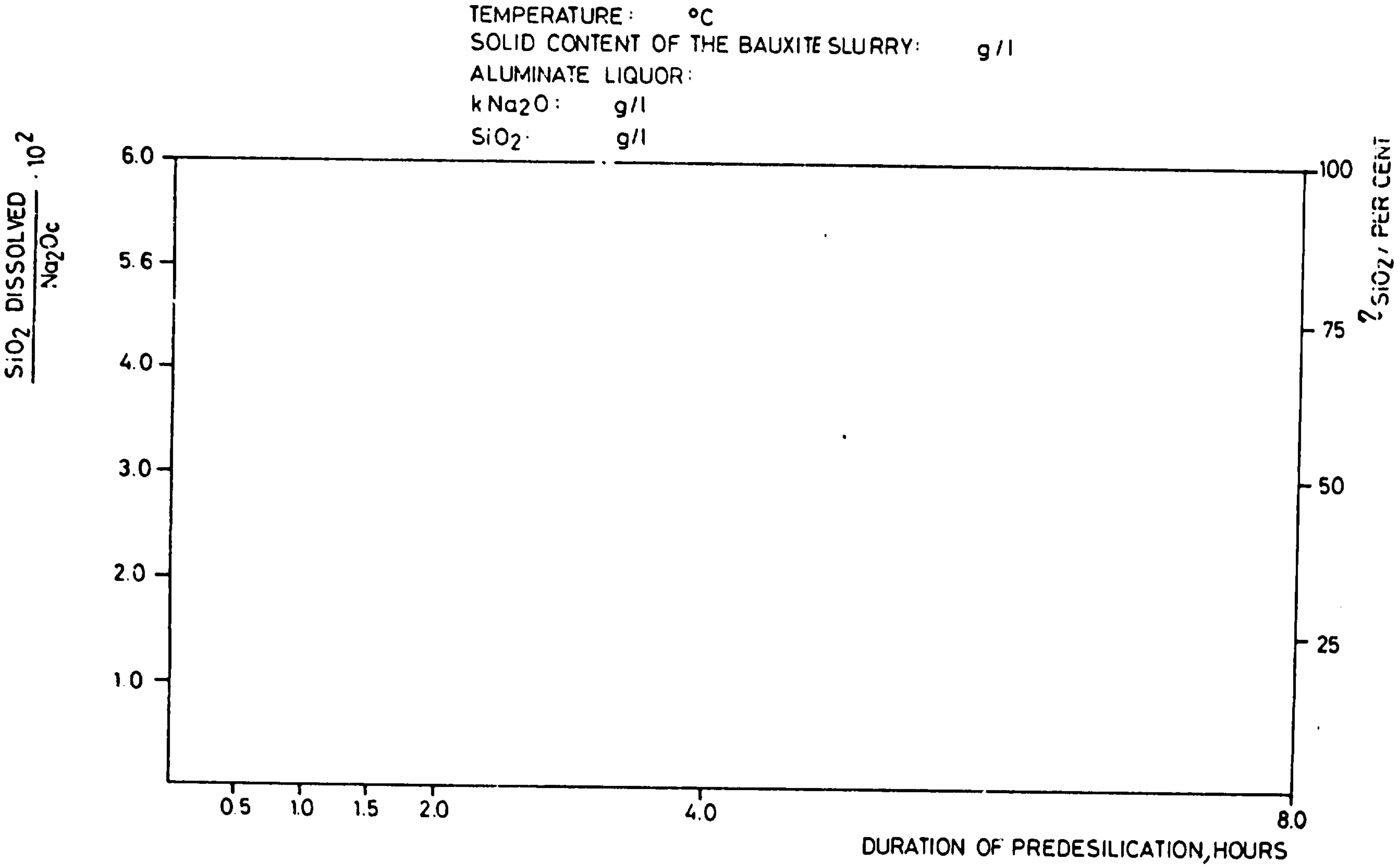


Fig. 8.11

EVALUATION OF PREDESILICATION TESTS

8. BAUXITE DIGESTION AND RED MUD SETTLING

THE OBJECTIVE OF DIGESTION TESTS

The aim of the digestion tests is to characterise the digestibility of bauxite samples, investigated during the previous practices, by plotting the caracteristic curves of digestibility.

Besides the optimization of the digestion parameters, the digestion tests are applied for investigating the following technological problems:

- optimization of the digestion paramters from the view--point of the phase-transformation of goethite to hematite
- optimization of the dosage of the digestion aids (e.g. CaO in the case of diasporic bauxites)
- production of red mud for further investigation.

This laboratory exercise includes the plotting of the characteristic curves of digestibility and the determination of the most important material ratios calculated on the basis of the digestion test only.

The digestion process can be modelled very well in laboratory.

LABORATORY EQUIPMENTS USED FOR DIGESTION TESTS

Laboratory autoclaves of 100-5000 cm^3 volume are made of steel, equipped by suitable stirrer and controlled or program--controlled heating are used for bauxite digestion modell tests.

A suitable volume of the experiment is chosen corresponding to the further experimental program following digestion.

In case the settling features or causticization of the red mud gained at the digesting process is examined, it is suitable to accomplish the digesting tests in a larger volume (some litres in vol).

When the only objective is the optimization of the digestion parameters and we need the aluminate liquor and the amount of the red mud for chemical analysis, it is enough to carry out the experiments in 100-200 cm^3 volume.

We give some illustrations in the following of the basic equipment most frequently used for alumina technological tests.

OIL-BATH EQUIPMENT FOR DIGESTION

The equipment is fit with thermostate controlled electric heating and filled with high flash-point oil. Six autoclave bombs can be placed in it. The autoclave bombs are turned by a rotary mechanism at 18-20 rev/min. speed in order to stir the material inside the bombs. The volume of autoclave bombs is 100-200 cm^3. The schematic drawing of the equipment is shown in Fig.8.12. The conception for sealing the autoclave bombs is illustrated in Fig.8.13. The oil-bath equipment for digestion can be used in a temperature range of 100-260 °C, mostly for investigation tests; e.g. for experiments, conducted for plotting the characteristic digestion curves.

The digesting temperature can be controlled in a range of ± 1 °C.

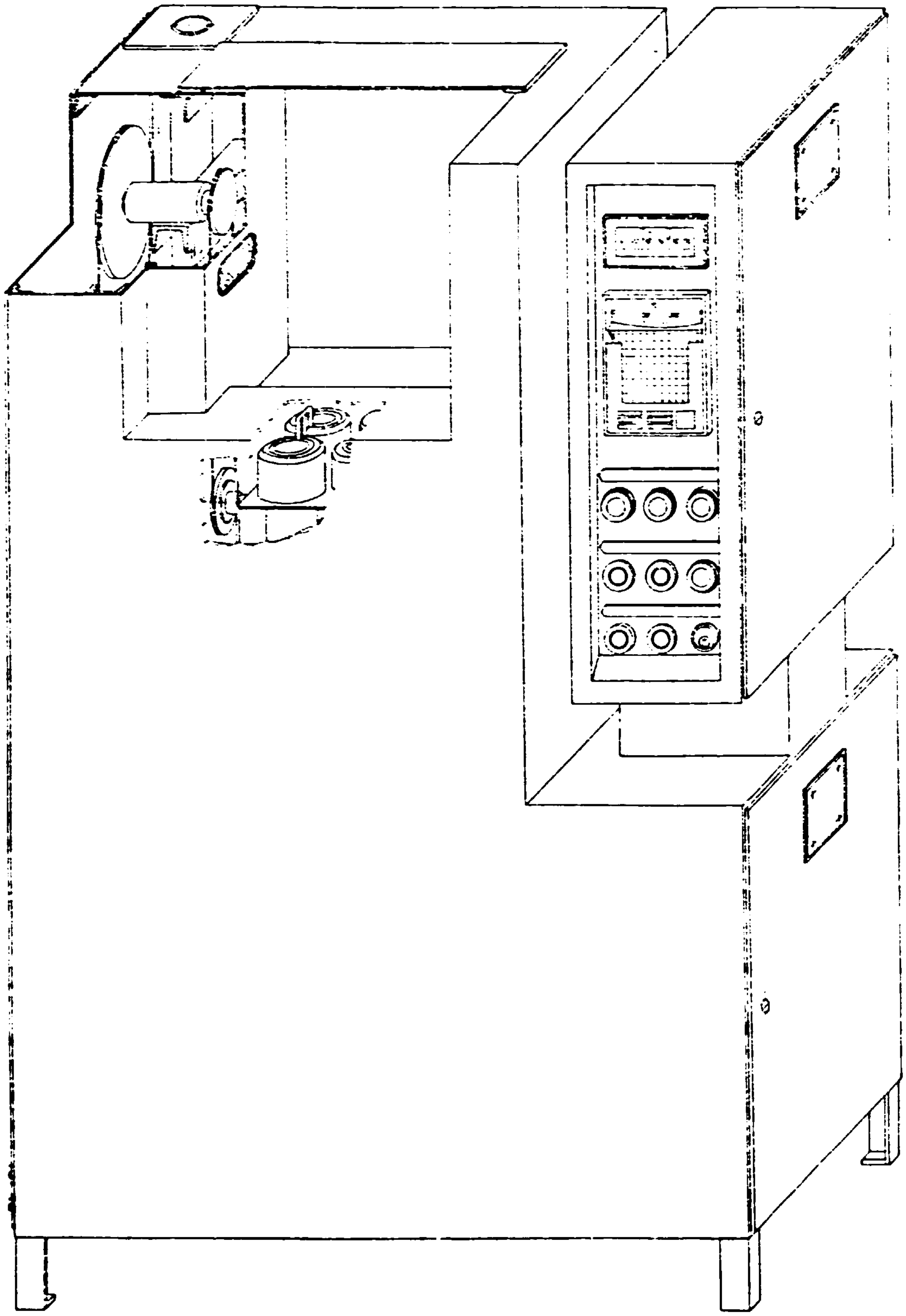


Fig. 8.12

OIL BATH EQUIPMENT FOR DIGESTION

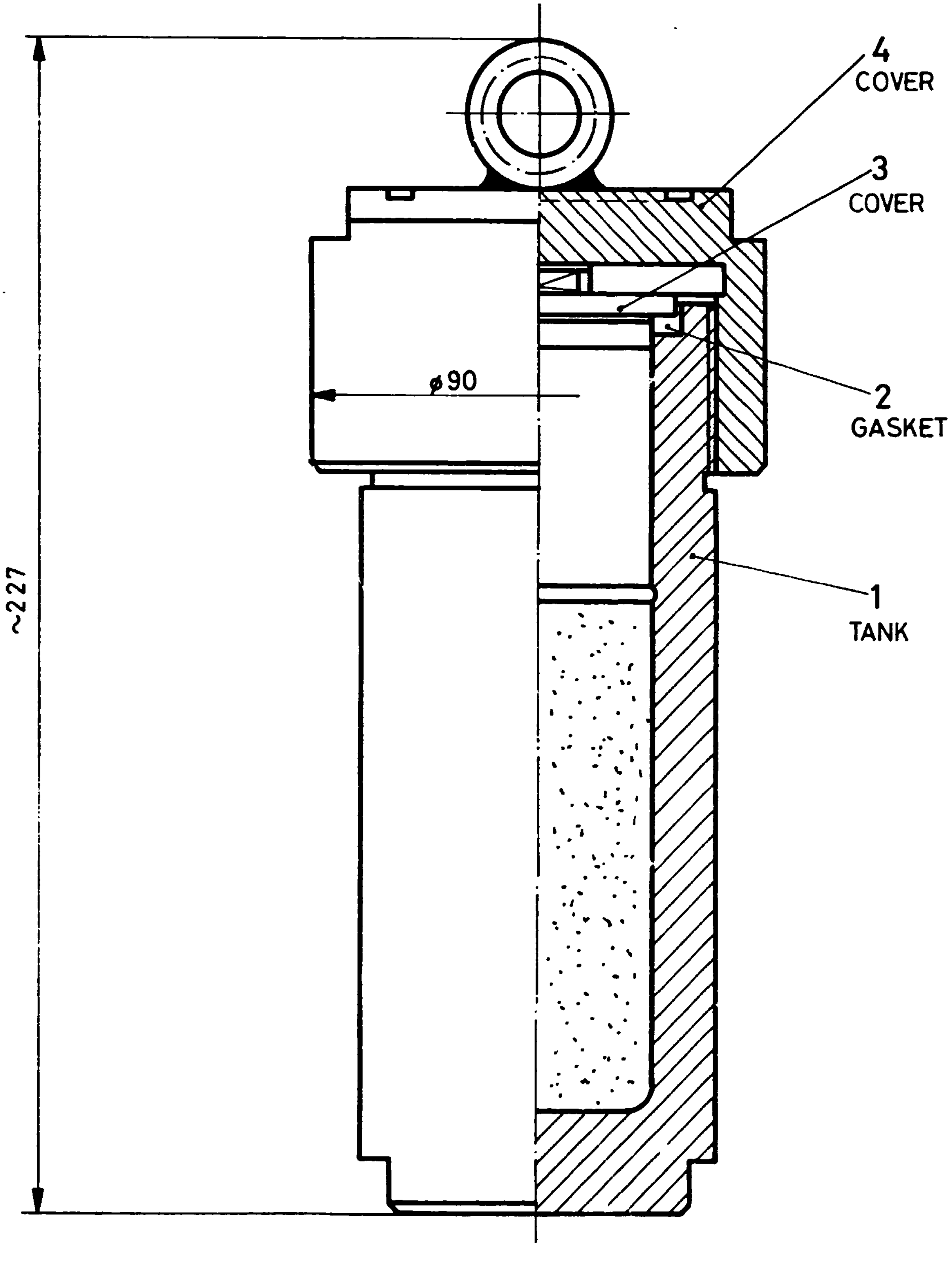


Fig. 8.13
AUTOCLAVE BOMB

Digestion tests can also be carried out in autoclave bombs rotated in salt-bath or air thermostate, in the same way.

AUTOCLAVE WITH MECHANIC STIRRER

Autoclaves (1000-5000 cm^3) equipped with mechanic stirrer, and by direct electric heating or placed in oilbath are used for laboratory digestion, in case a larger amount of slurry required. The section drawing of an autoclave of this type is illustrated in Fig.8.11.

DIGESTING EQUIPMENT FOR DIGESTION ON EXTREME HIGH TEMPERATURE (> 250 °C)

The apparative development of bauxite digestion progresses more and more in the direction of high temperature digestion and the application of tube-reactor. So the high temperature digestion is often needed for laboratory modelling.

The applied equipment for modelling high temperature processes (250-350 °C) is shown in Fig.8.15.

The equipment consists of an aluminium cylinder rotating round the horizontal shaft which is supplied with controlled--electric heating. Six autoclaves (200 cm^3 vol.each) can be put into the holes of the cylinder.

PLANNING OF DIGESTION TESTS

The optimum parameters of digestion are to be determined by digestion tests of different bauxites. The chemical and mineralogical composition of the bauxites are known from the bauxite analyses (1-5 exercise), and the most important specific data have to be determined on the basis of digestion test.

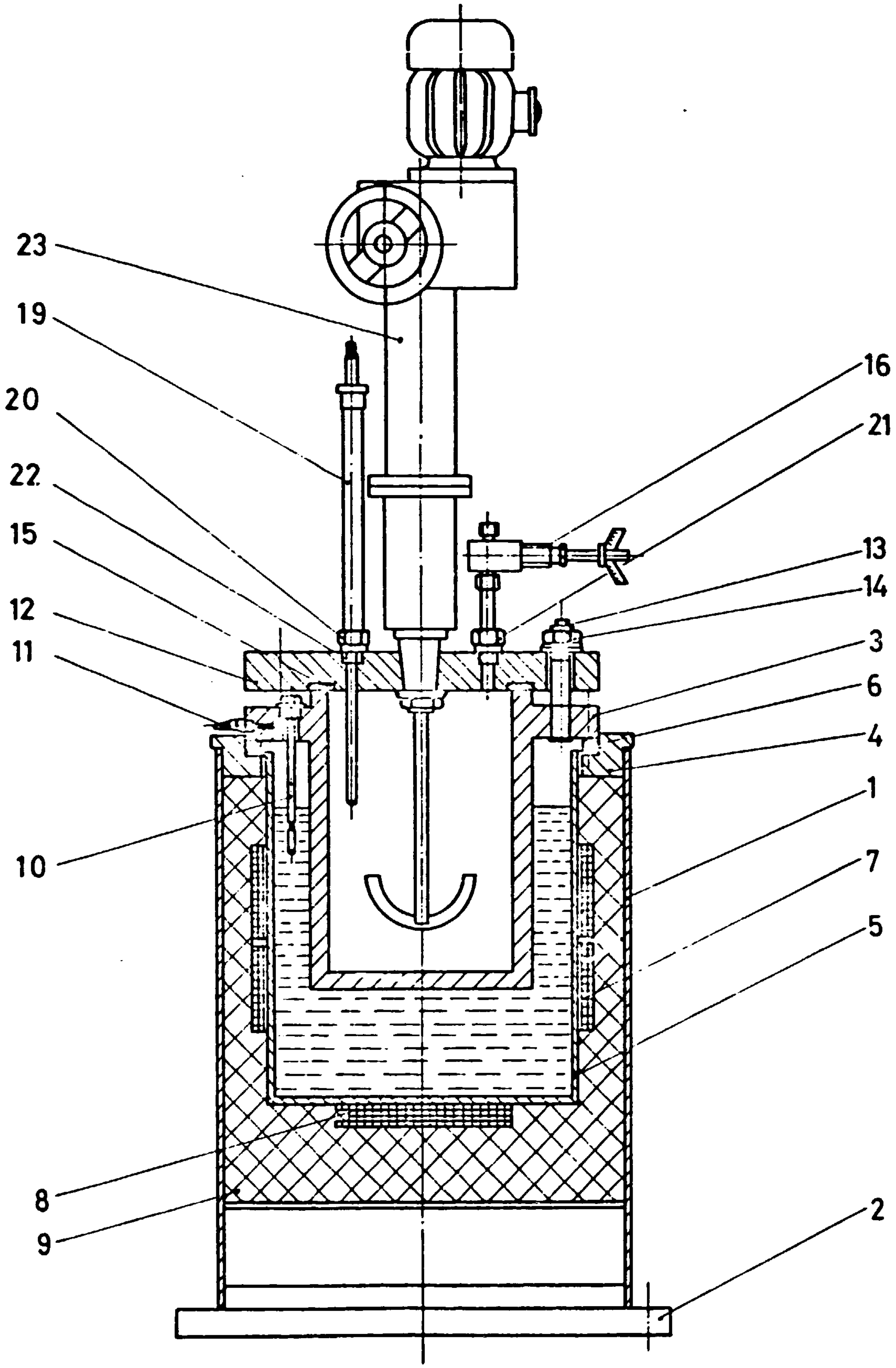


Fig. 8.14

LABC RATORY AUTOCLAVE SUPPLIED WITH MECHANIC STIRRER

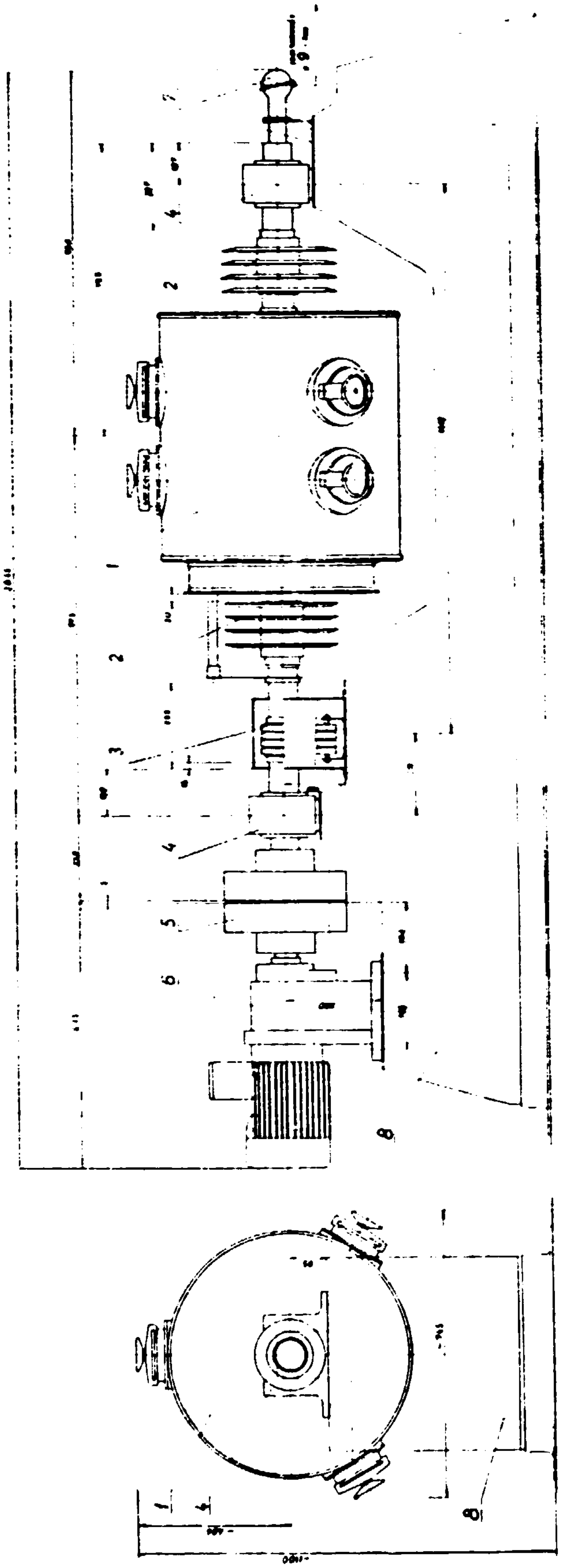


Fig. 8.15

DIGESTING EQUIPMENT FOR EXTREME HIGH TEMPERATURE

Each group has to perform the digestion test with the bauxite samples they analysed before (1-5 exercise).

Each group has to determine on the basis of the test results of bauxite, the mineralogical type of the prepared bauxite sample (gibbsitic, boehmitic, diasporic).

On the basis of the diagram on the equilibrium solubility of aluminium minerals given in Volume 6, the approximate optimum of digestion temperature and liquor concentration is to be shown. The characteristic curve of digestibility characterising the digestibility of the bauxite sample is to be plotted by application of the chosen digestion temperature and liquor concentration.

The ratio of digestion liquor necessary for the required aluminate liquor-molar-ratio after the digestion, can be calculated as follows.

We determine the so called liquor figure i.e. the required amount of NaOH (expressed in Na_2O), necessary to digest 1 kg bauxite, supposing theoretical recovery of the alumina $Na_2O \cdot Al_2O_3 \cdot 1.7SiO_2 \cdot H_2O$ composition for the Na-Al-silicates and α_a caustic molar ratio after digestion.

$$N = 0.608\,\alpha_a\,(a-S) + 0.608\,S \qquad (8.1)$$

where:

N : liquor figure
α_a : the required molar ratio after digestion
a : Al_2O_3 content of bauxite, g Al_2O_3/kg bauxite
S : reactive SiO_2 content of bauxite, g SiO_2/kg bauxite

The active NaOH content of the digestion liquor expressed in Na_2O can be determined by the following formule:

$$Na_2O_{active} = \frac{C_k(\alpha_o - \alpha_a)}{\alpha_o} \qquad (8.2)$$

where:

C_k : caustic Na_2O content of digestion liquor, gpl
α_o : caustic molar ratio of digestion liquor
α_a : required molar ratio of the aluminate liquor

Taking into account the two expressions given above: the required amount of bauxite for 1 l digesting liquor can be calculated by the following formule suppose the required molar ratio is α_a:

$$G = \frac{C_k(\alpha_o - \alpha_a)}{N\alpha_o} = \frac{C_k(\alpha_o - \alpha_a)}{\alpha_o . 0.608 . \alpha_a (a-S) + \alpha_o . 0.608S} \text{ kg} \qquad (8.3)$$

Based on the above relationship let us calculate now the weights of bauxite necessary for plotting the characteristic digestion curve, with regard to the mineralogical type and chemical composition of the bauxite and concentration of the digesting liquor.

The volume of the digestion liquor is 150 cm^3 in each experiment.

The bauxite weights for the six bombs digestion test series are calculated for the following molar ratios (α_a):

1.2; 1.3; 1.4; 1.5; 1.6; 1.8

In case of diasporic bauxite 3 % CaO is added in each experiment, calculated for the weight of dry bauxite.

PERFORMANCE OF THE DIGESTION TEST

Switch on the oil-bath digestion equipment and heat it up to 100 °C, pour 150 cm^3 of digesting liquor of given concentration (plant liquor possibly) in each of the autoclave bombs. Add the quantity of bauxite - quantity of CaO in case of diasporic bauxites - (counted as written in 8.3) to the digestion liquor, charged in order of increasing molar ratio (decreasing weight of bauxite). After that stir the suspension well with a glass-rod. Check the sealing of the bombs! Then put the autoclave bombs into a special vice made for fastening the lids to the bombs.

Put the sealed autoclave bombs into the oil-bath equipment and fix them well. After we had been convinced that the autoclave bombs are fixed well, switch on the rotator, and start to heat the bath to the required digestion temperature. After attaining the required digestion temperature, continue the digestion for 20 minutes in case of gibbsitic bauxite, for 60 minutes in case of boehmitic and diasporic bauxites. When the digestion is finished, switch off the rotator, take out the autoclave bombs, put them on the edge of the oil-bath equipment. After 4-5 minutes cool the autoclave bombs with running cold water to 50-60 °C. After cooling open the autoclave bombs and separate the aluminate liquor from the red mud content of the digested slurry by centrifuge. Centrifugation is carried on for 10 minutes at 3000 rev/min. velocity. Separate the aluminate liquor for analysis.

Analyse the caust. Na_2O and Al_2O_3 content of the aluminate liquor. Wash the red mud samples in the following way.

Prepare a diluted solution (Na_2O_{total} = 2 gpl concentration) from the digestion plant liquor used for the digestion test and heat it to the boiling point. It corresponds to the concentration of the liquid phase of well treated red mud in the end of the washing line.

After removing the aluminate liquor, repulp the remaining red mud intensively in each of the cells with 400-500 cm^3 diluted solution made as above. Then centrifugate again and after centrifugation pour out the caustic wash liquor.

Repeating the repulpings and centrifugation three times, put the separated red mud into a dryer to dry on 110 ^oC for a night.

After drying prepare and grind the red mud minus 100 μm for chemical analysis and minus 63 μm for X-ray investigation.

The following chemical components have to be determined in the red mud of the digested bauxite:

Fe_2O_3
Al_2O_3
SiO_2
TiO_2
L.O.I.
Na_2O_{total}
CaO
MgO

The analysis is to be completed by atomic absorption spectrophotometric method.

Take X-ray diffractograms of all the six red mud samples of the digestion test.

EVALUATION OF THE EXPERIMENTS

RECOVERY CALCULATION

On the basis of the chemical composition of the bauxite and red mud, calculate the Al_2O_3 recovery of digestion at all the six experiments using the following formule:

$$= \frac{(Al_2O_3)_{bx} - \dfrac{(Fe_2O_3)_{bx} \cdot (Al_2O_3)_m}{(Fe_2O_3)_m}}{(Al_2O_3)_{bx}} \cdot 100 =$$

$$= \left[1 - \frac{(Al_2O_3)_m \cdot (Fe_2O_3)_{bx}}{(Al_2O_3)_{bx} \cdot (Fe_2O_3)_m} \right] \cdot 100 \ \%$$

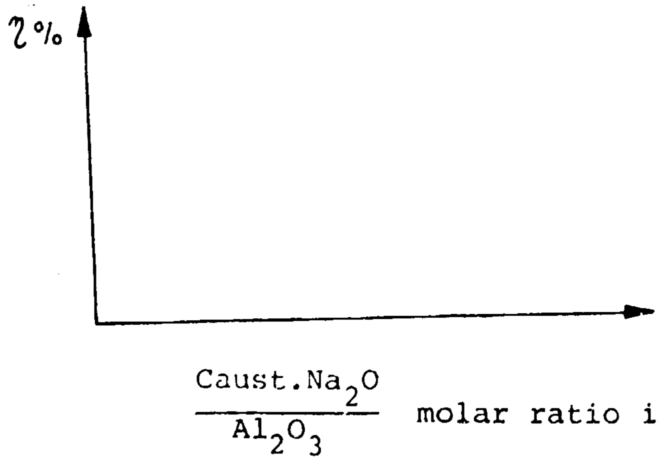
The computation is based on the equal amount of Fe_2O_3 both in the bauxite and the red mud.

In brackets Fe_2O_3 and Al_2O_3 content of the bauxite (bx) and red mud (m), wpct.

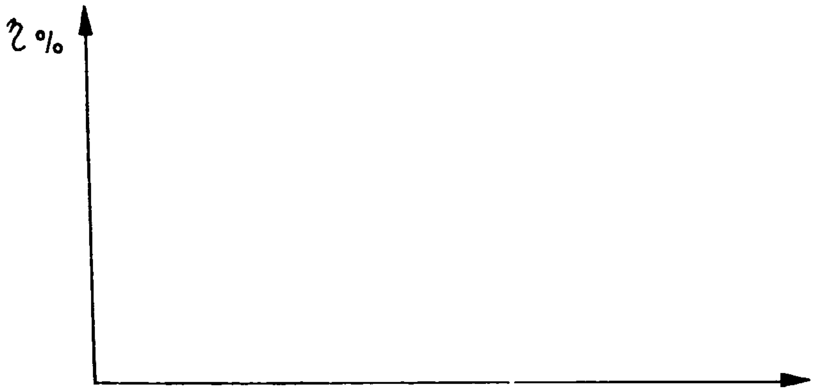
PLOTTING THE CHARACTERISTIC CURVE OF DIGESTION

Construct the characteristic curve for digesting on the basis of the experimental data of the investigations.

According to Europian practice



According to American practice



$\frac{Al_2O_3}{caust.Na_2CO_3}$ weight ratio in aluminate liquor

caust.Na_2CO_3 = 1.7096 caust.Na_2O (causticity expressed in sodium-carbonate)

DETERMINATION OF THE OPTIMUM MOLAR RATIO AFTER DIGESTION

Determine the optimum molar ratio after digestion on the basis of the characteristic curves of digestibility according to the American and Europian nomenclature.

DETERMINATION OF THE Na_2O/SiO_2 MOLAR RATIO

On the basis of the chemical composition of the red mud determine the Na_2O/SiO_2 molar ratio characteristic to the bound soda losses, by the following formule:

$$\frac{Na_2O}{SiO_2} \text{ molar ratio} = \frac{Na_2O\ \%}{SiO_2\ \%} \quad \frac{60}{62}$$

% wpct of red mud.

DETERMINATION OF THE SPECIFIC BAUXITE CONSUMPTION

From the characteristic curve of digestibility, determine the alumina recovery corresponding to the optimum molar ratio after digestion. After that determine the specific consumption of dry bauxite by the following formule:

$$Q = \frac{990}{\eta' . a} \qquad \text{(t/t alumina)}$$

where:

Q : the weight of dry bauxite (t) needed for producing 1 t alumina (if no other losses would occur after digestion)

η' : $\frac{\eta \%}{100}$

a : Al_2O_3 content of bauxite, kg/t

The equation relates to 99 % Al_2O_3 in alumina product.

DETERMINATION OF SPECIFIC RED MUD PRODUCTION

On the basis of the determined specific bauxite consumption and the chemical compositions of bauxite and red mud, calculate the quantity of the produced red mud for the production of 1 t alumina, by the following formule:

$$G = Q \frac{Fe_2O_{3\ bx}\ \%}{Fe_2O_{3\ m}\ \%} \qquad \text{(t/t alumina)}$$

where:

bx: bauxite

m : red mud

DETERMINATION OF THE BOUND Na_2O AND Al_2O_3 LOSSES

Determine the loss of the bound NaOH and Al_2O_3 referred to 1 t alumina product on the basis of the determined specific red mud production and the chemical composition of the red mud by the following formule:

$$W_{NaOH} = G\ (Na_2O_m)\ .\ 12.9 \quad \text{(kg NaOH/t alumina)}$$

$$\frac{2NaOH}{Na_2O} = \frac{80}{62} = 1.29$$

$$W_{Al_2O_3} = G\ (Al_2O_{3\ m})\ .\ 10 \quad \text{(kg } Al_2O_3\text{/t alumina)}$$

In the brackets Al_2O_3 and Na_2O content of red mud, wpct.

STUDYING OF THE MINERALOGICAL COMPOSITION OF RED MUD

Complete an X-ray quantitative analysis of the six red mud samples gained from digestion tests and compare the diffractograms for examining the remained quantity of undegisted aluminium minerals.

RED MUD SETTLING TEST IN SETTLING TUBE

The designing parameters of red mud settlers are gained from γ-ray absorption settling tests (chapter 9.). However, quick, comparative evaluation can be made in the considerable more simple settling tube.

The tube settling experiments are carried out in a mm scaled settling tube of 30 cm height and 130 ml volume put into a suitable transparent walled thermostate vessel.

This method is suitable to compare red muds obtained from different bauxites or digested by different technologies, or to determine the effects of different flocculant aids.

EXERCISE

Test the behaviour of red mud sample of Iszkaszentgyörgy bauxite, prepared for this exercise, at using different flocculant aids.

FLOCCULANT DOSAGES

1. Without flocculant
2. 2 kg flour per t red mud
3. 50 g ALCLAR-500 per t red mud
4. 150 g ALCLAR-500 per t red mud
5. 50 g NALCO SC-81-09 per t red mud
6. 150 g NALCO SC-81-09 per t red mud
7. 50 g CYANAMID RMR-50 per t red mud
8. 150 g CYANAMID RMR-50 per t red mud

Homogenize properly the slurry of known solid concentration prepared in advance and fill it into the settling tubes. Put the settling tubes into a water bath thermostated at 95 °C for about 15 minutes to take up the bath temperature, weigh the amounts of flocculant solutions into the tubes and homogenize the slurry in the settling tube. Read the mud level height at each settling tube at settling times: 1', 2', 5', 10', 15', 20', 30', 40', 50', 60'.

EVALUATION OF THE RESULTS

1. Plot the mud level height in the function of settling time at each test.
2. Compare the effect of applied flocculants (settling ratio, compactivity, clear zone clairity).

9. MEASUREMENT OF RED MUD SETTLING BY γ-RAY ABSORPTION

The Soft-Gamma-ray Absorption Model Settler (SAM) unit serves for registering the solids concentration profiles developing in the course of static settling of red mud suspensions, in the function of time (Fig.8.16.).

In case of a narrow ray-beam, the radiation intensity is the exponential function of the solids concentration:

$$I_c = I_o \, . \, \exp. \, (-a.c) \qquad (1)$$

In order to determine the concentration scale, the c_o initial solids concentration has to be determined in each settling test by the traditional method, that is, by measuring the weight of the solids content of a slurry of known volume. The equation (1) is also valid for c_o initial concentration:

$$I_c = I_o \, . \, \exp. \, (-a.c_o) \qquad (2)$$

The concentration scale is obtained by relating the equations no (1) and (2):

$$I_c = I_o \left| \frac{I_o}{C_o} \right|^{\frac{c}{c_o}} \qquad (3)$$

Distance data proportional to the radiation intensity can be read off the registrate (x_o; x_c; x_{c_o}), and these data have to be used for the calculations:

$$I_c = x_o \left| \frac{x_o}{x_{c_o}} \right|^{\frac{c}{c_o}} \qquad (4)$$

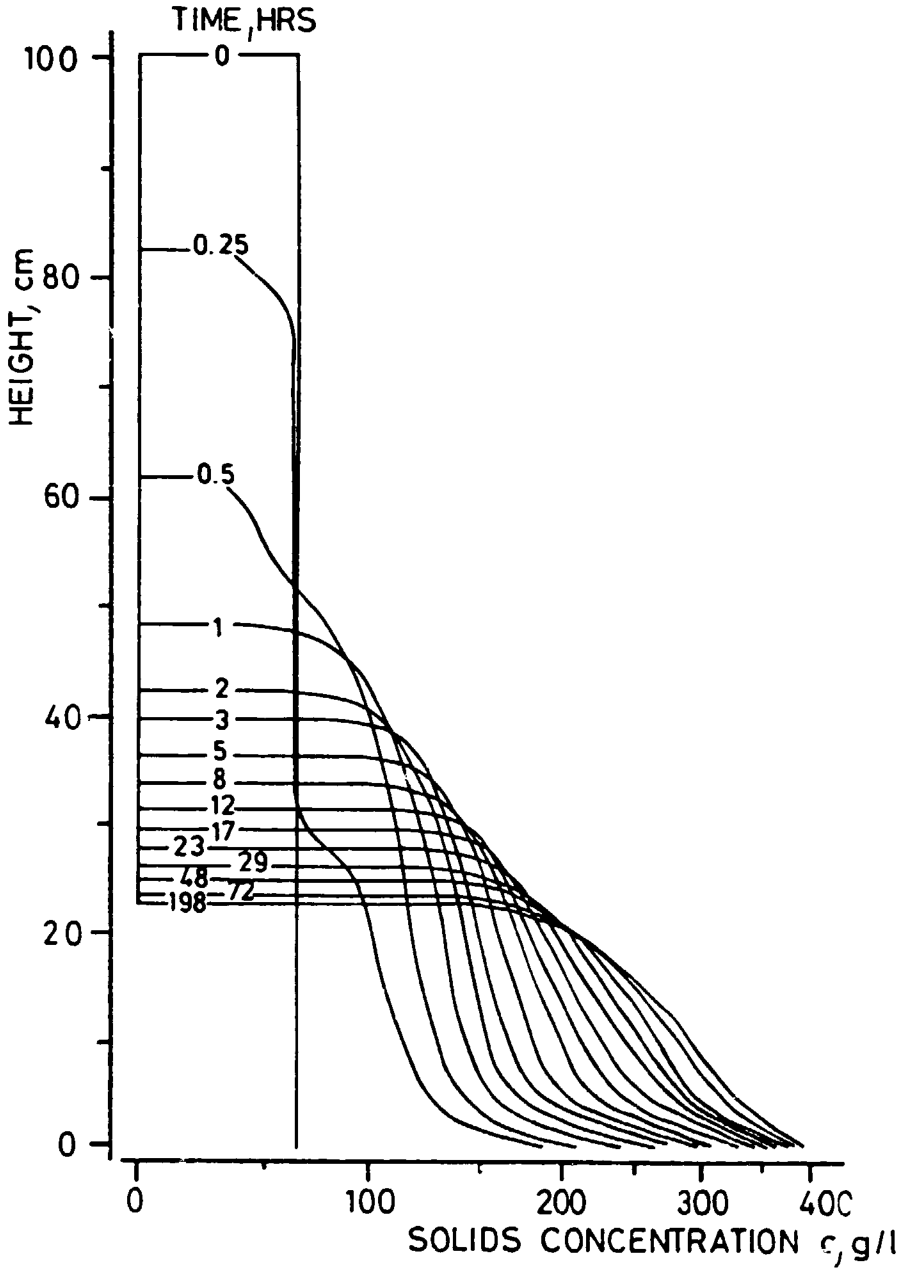


Fig. 8.16

SOLIDS CONCENTRATION PROFILES OF A RED MUD SLURRY TAKEN BY THE SEDIMENTATION APPARATUS

From a series of concentration profiles taken during sedimentation, the settling velocity of the solid u_c in a pulp layer of c concentration can be determined. Fig.8.17 shows a detail of the concentration profiles, among others, two ones taken at the time t and t+Δ resp. The vertical line drawn at c crosses the profiles at points z_c and $(z+\Delta z)_c$.

The layer of concentration c migrates upward at a velocity of

$$U_c = \frac{\Delta z}{\Delta t} \tag{5}$$

The amount of solids passing through the layer during t with a settling rate of u_c

$$m = (U_c + u_c)\ c\ \Delta t \tag{6}$$

m can be determined from the concentration profiles as a difference of areas $O(z+\Delta z)_c$ EH and Oz_cFG. Mark the shaded area in Fig.8.17 by A, then

$$m = c\Delta z + A \tag{7}$$

From Eqs (5) to (7), the settling velocity in a layer of concentration c is

$$u_c = A/c\Delta t \tag{8}$$

The solids flux can be calculated in the fuction of the concentration, by the following formula:

$$S = c\ .\ u_c \tag{9}$$

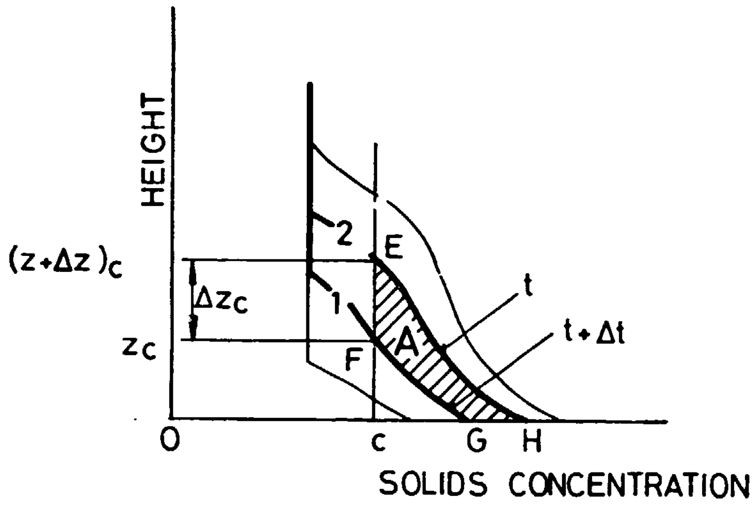


Fig.8.17

DETERMINATION OF u_c FROM THE CONCENTRATION PROFILES

The influence of solids concentration on the settling velocity is taken into consideration in the Richardson-Zaki equation:

$$u_c = u_o \, (1 - \mathcal{E})^n \tag{10}$$

where:

u_o : Stokes settling velocity
$\mathcal{E}$: relative solids concentration of slurry, $\mathcal{E} = c/\rho_s$
n : empirical constant depending on the Reynolds number

Taking into account the solvatation and floc structure, the following formula was obtained by Michaels and Bolger:

$$u_f = u_o \, (1 - kc)^{4.65} \tag{11}$$

where:

u_f : observed settling rate of the slurry-interface of concentration c
u_o : Stokes settling velocity of an average floccule
k : volume of floccules produced by unit weight of dry solid

Introducing the solvatation factor α as a quotient of the volume of an average floc (V) and the average volume of solids (v) in the floc

$$\alpha = V/v;$$

hence

$$kc = \alpha \mathcal{E} \tag{12}$$

For ideal suspensions $\alpha = 1$.

Eq. (11) is valid for the velocity of the slurry-interface of the pulp during settling in a narrow concentration interval around the c_o initial concentration. With the well known Stokes-velocity equation, the following formula is obtained for the settling rate at c_o initial concentration

$$u_{co} = \frac{\bar{D}^2 (\rho_s - \rho_l) g}{18 \eta \alpha} (1 - \alpha \mathcal{E})^{4.65} \qquad (13)$$

where:

u_{co} : settling rate of the slurry-interface of pulp of c_o concentration

Our experimental technique allowed us to determine the settling rate in the slurry too, i.e., the velocity of particles passing through a layer of c solids concentration. It was proved that Eq. (13) is also valid for all c concentrations that occur in the pulp during settling.

From Eqs (11) and (13)

$$u_c^{1/4.65} = -\frac{\alpha u_o^{1/4.65}}{\rho_s} c + u_o^{1/4.65} \qquad (14)$$

and

$$\bar{D} = \left(\frac{18 \eta \alpha u_o}{(\rho_s - \rho_l) g} \right)^{1/2} = \left(\frac{510 \alpha u_o \eta}{\rho_s - \rho_l} \right)^{1/2} \qquad (15)$$

Having determined the velocity vs. concentration relation (Fig.8.18) i.e., u_c as a function of c, u_o is given as the intercept of the ordinate, solvatation factor α as the quotient of the intercept of the abscisse and the solids density, and the average diameter of flocs $\bar{D}$ can be calculated from Eq. (15).

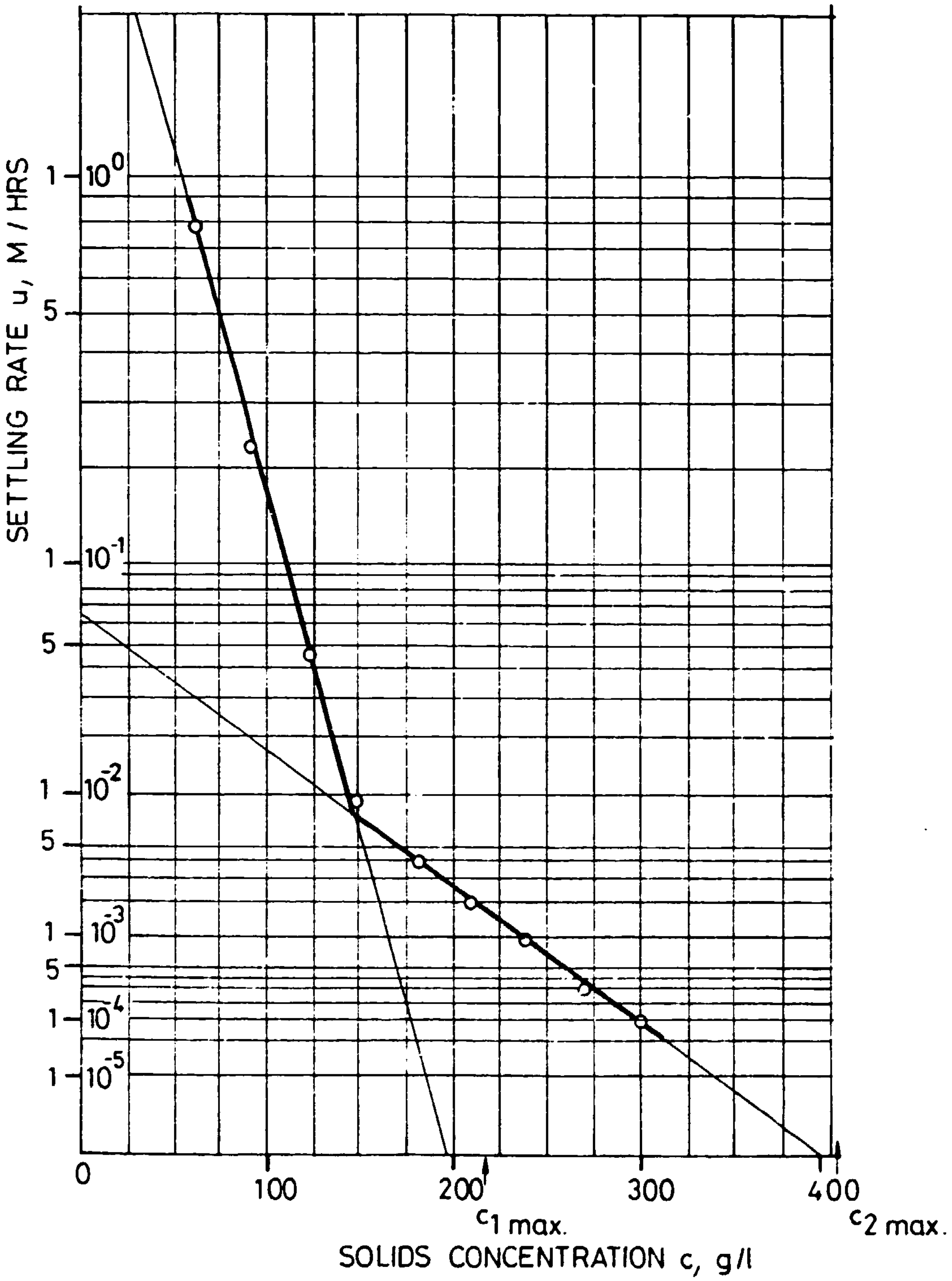


Fig. 8.18

THE uc-c RELATIONSHIP FOR RED MUD SLURRIES

PRACTICAL EXERCISES

Members of the exercise take part in carriing out a SAM settling test. They get the profile series of a red mud settling concentration registered formerly.

1. Determine the concentration of the registrate's abscisse, based on equation (3) if c_o is given.

2. Draw the H-t diagram, after reading the eventual mud level off the profile curves. Determine the initial settling velocity of the mud level (u_o).

3. Draw into the H-t diagram the vertical position of the layers having different solids concentrations, in the function of the settling time. Determine the velocity of upward migration (U_o) of these concentrations /Eq.(5)/.

4. Determine the average compactness of mud settled during 24 hours and the compression, i.e. the quotient of the above value and that of the initial solids concentration, c_o.

5. Determine the solids flux (9) and the settling velocity (8) vs. concentration by the help of a Hewlett-Packard calculator, according to Fig.8.17.

Using the data, plot the batch flux diagram and the velocity diagram.

6. Determine the characteristic flocculant parameters from both straight sections of the velocity diagram (u_{o1}; D_1; α_1; u_{o2}; D_2; α_2).

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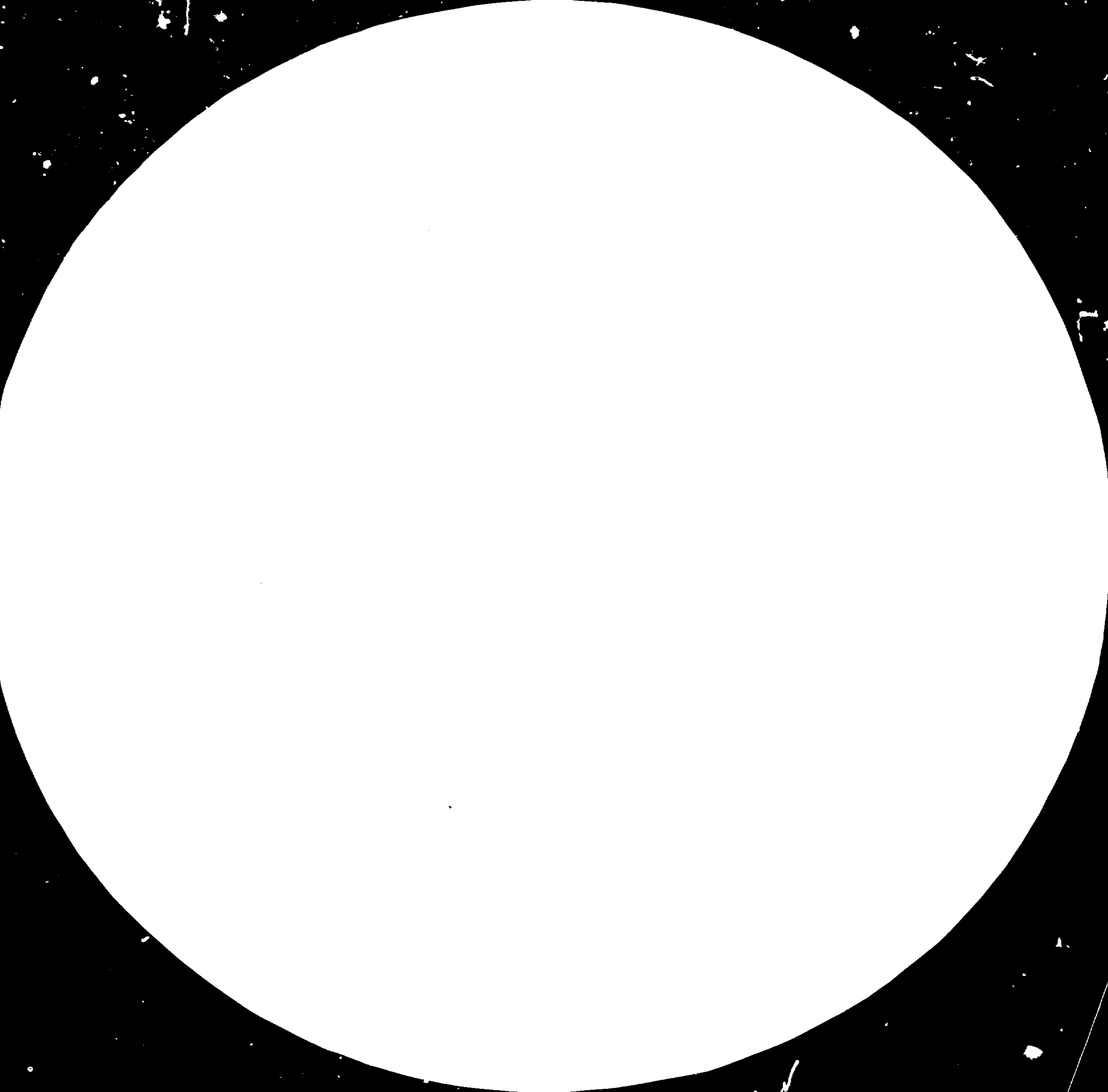
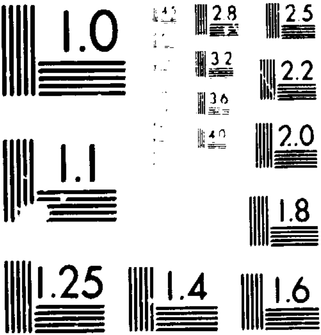




MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS 1963 A

10. DETERMINATION OF MAIN COMPONENTS OF RED MUD BY AAS AND FLAME PHOTOMETRIC METHOD

DETERMINATION OF MAIN COMPONENTS OF RED MUD BY AAS ANALYTICAL SYSTEM

Main components of bauxite and red mud can regularly be determined by wet chemical methods written down in Chapter 5.

In case of quick technological control, the application of AAS (atomic absorption spectrophotometry or analytical atom spectrometry) method to determine the main components of red mud and bauxite is favourable for evaluation of different digestion experiments due to its suitable reproducibility, less time- and sample consumption as well as economic operation costs.

Principle: The solution of red mud samples made by fusion of sample with strontium carbonate-boric acid flux and solved in diluted hydrochloric acid is sprayed to a flame selected according to the component to be determined. In the flame, the absorption of the resonant light of the selected hollow cathode lamp is proportional to the concentration of the component in the sprayed solution. The parts of our AAS analytical system are: changer, SP 1900 AAS instrument, a Solatron data transfer unit, a Facit punch tape and a Hewlett-Packard 9830 table calculator. The flow-chart of this system can be seen in Fig.8.19a.

The intensity data of AAS are recorded on a punch tape and fed to the calculator. The result is printed as laboratory report by a Facit typewriter controlled by the calculator.

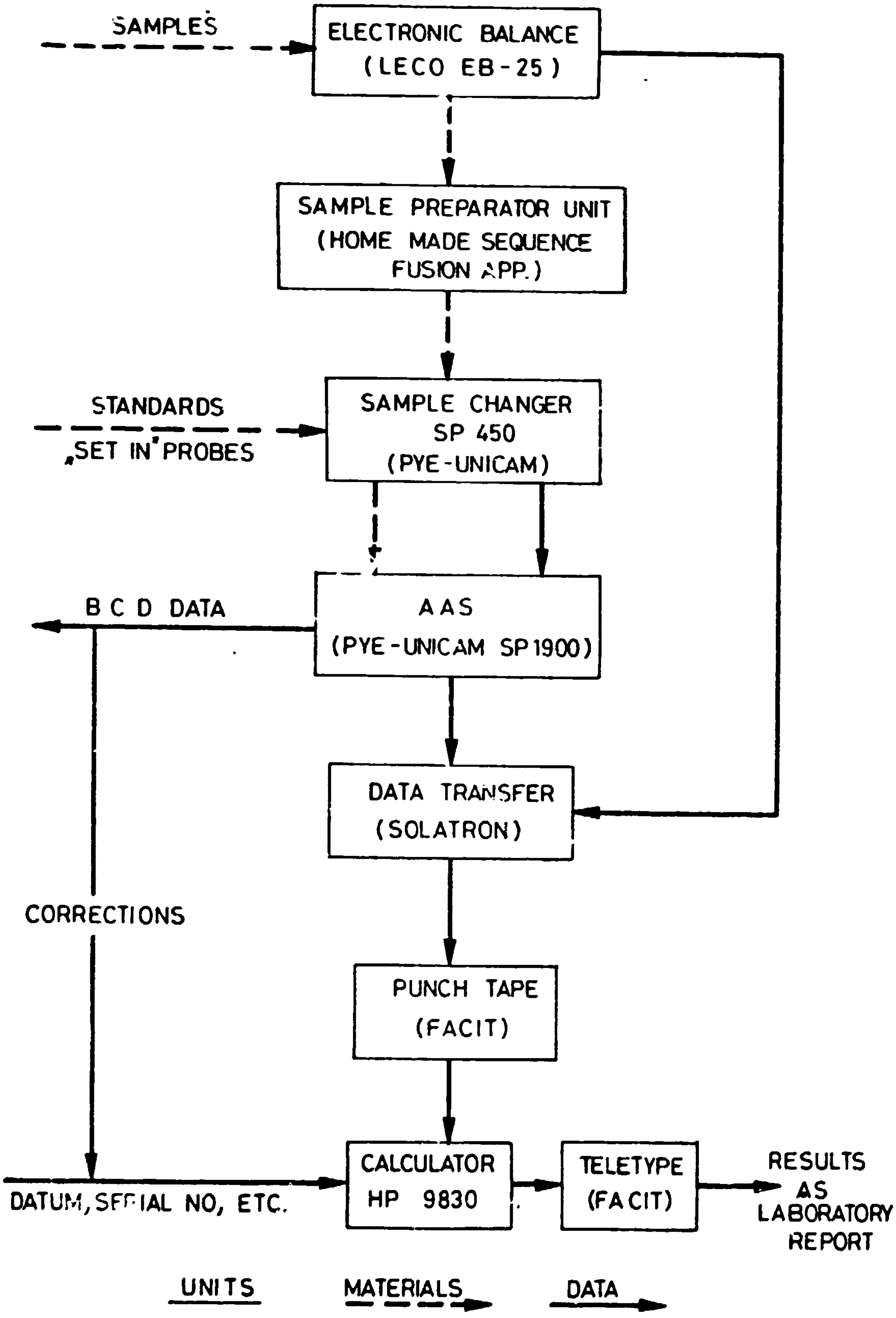


Fig. 8.19a
FLOW CHART

PROCEDURE

SAMPLE PREPARATION

Weigh in 0.2 g of six different air-dry red mud samples to platinum crucibles and 2 g of flux (1:1 mixture of strontium carbonate and boric acid). Take the crucibles to the sequence fusion apparatus after ignition of both flames. Set the temperature of both flames with the required selection of the ratio of town gas and oxygene and with the position of the valve of preheating flame. Select proper fusion time with the two knob of the electronic time selector (about 3-5 minutes in the case of red mud samples). Switch on the fusion apparatus and wait about half an hour till the fusion is performed. Take the crucibles to 200 ml beakers containing 10 ml of cc. hydrochloric acid and 100 ml of distilled water. Let the mixture dissolve from the crucible without heating and transfer the solution to a 200 ml volumetric flask washing the beaker and crucible with distilled water and fill to the mark.

Place clear cups to the tray of sample changer and pour the sample solutions, "set in" probe solutions and standard solutions as well as distilled water to the fifty cups according to the given order. The five standard solutions consist of required quantity of flux, hydrochloric acid and different volume of the El, Ti, Si, Ca and Mg stardard solutions 1 to 5 in growing order. The third standard solution can be used as "set in" probe. For the checking of the operation of AAS analytical system one of standard red mud sample solutions with known composition is applied on each tray.

Water	1, 4, 6, 8, 10, ... 46, 48, 50
Blank solutions	2, 15
Standard solutions	3, 5, 7, 9, 11, 13
Set in probes	3, 9, 23, 31, 39, 47

Sample solutions	17, 19, 21, 25, 27, 29, 33, 35, 37, 41, 43, 45
Standard sample solution	49

Order of samples: blank, standard solutions and water on the tray of the sample changer.

INSTALLATION OF AAS INSTRUMENT

After becoming familiar with the construction an operation of the AAS switch on the main instrument (SP 1900) the sample changer, data transfer unit and the punch tape. The basic installation of these instruments can be studied in the proper instruction manual.

Control the acetylene, compressed air and nitrous oxide gas supply and set the reducing valves and gas control valves to the required positions. (As the acetylene-air and acetylene-nitrous oxide mixtures can be dangerously explosive never leave the instrument unattended with the flame burning. A proper exhausting system can be applied since toxic heavy metal vapors and product may be formed.)

Turn the lamp selector knob to the required position for the selection of lamp of the element to be determined, set the suitable lamp current and find the element line by turning the monochramotor control to the required wavelength. Ignite and adjust the flame according to the element to be determined. (In the case of Al, Si, Ti and Ca acetylene-nitrous oxide flame can be used.)

Aspirate the "set in" probe solution to the flame and select the required sensitivity by turning the scale expansion knob in concentration mode.

WORKING PROCEDURE

Set the sample changer to position 1 of tray and take the aspirating capillary to the sampling arm. Select the 4 sec integration interval, start the sample changer operation in double mode, and start data transfer and punch tape and wait till all the fifty sample are aspirated. The operation of instruments can be controlled watching the read out in the display.

Change the lamp and flame conditions for the next element, select the required sensitivity and repeat the previous sequence of procedure. The suitable order of elements to be determined is: Al, Si, Ti, Ca, as well as Fe and Mg because of the change of burning mixture from acetylene--nitrous oxide to acetylene-air.

CALCULATIONS

Collect the weight, loss on ignition and sodium content data from other experiements. Take the punch tape with the recorded intensity data and use the HP 9830 computer according to the user manual and the program manual. The main steps of evaluating program can be seen in Fig.8.19b. The results as a laboratory report is printed with the selected printer.

PRECISION

Variation coefficient	Element to be determined
1	Al
3	Si
3	Ti
3	Ca
1	Fe
3	Mg

700 DATA /6 samples/ DAY WITH APPLICATION OF A COMPUTERIZED DATA PROCESSING SYSTEM.

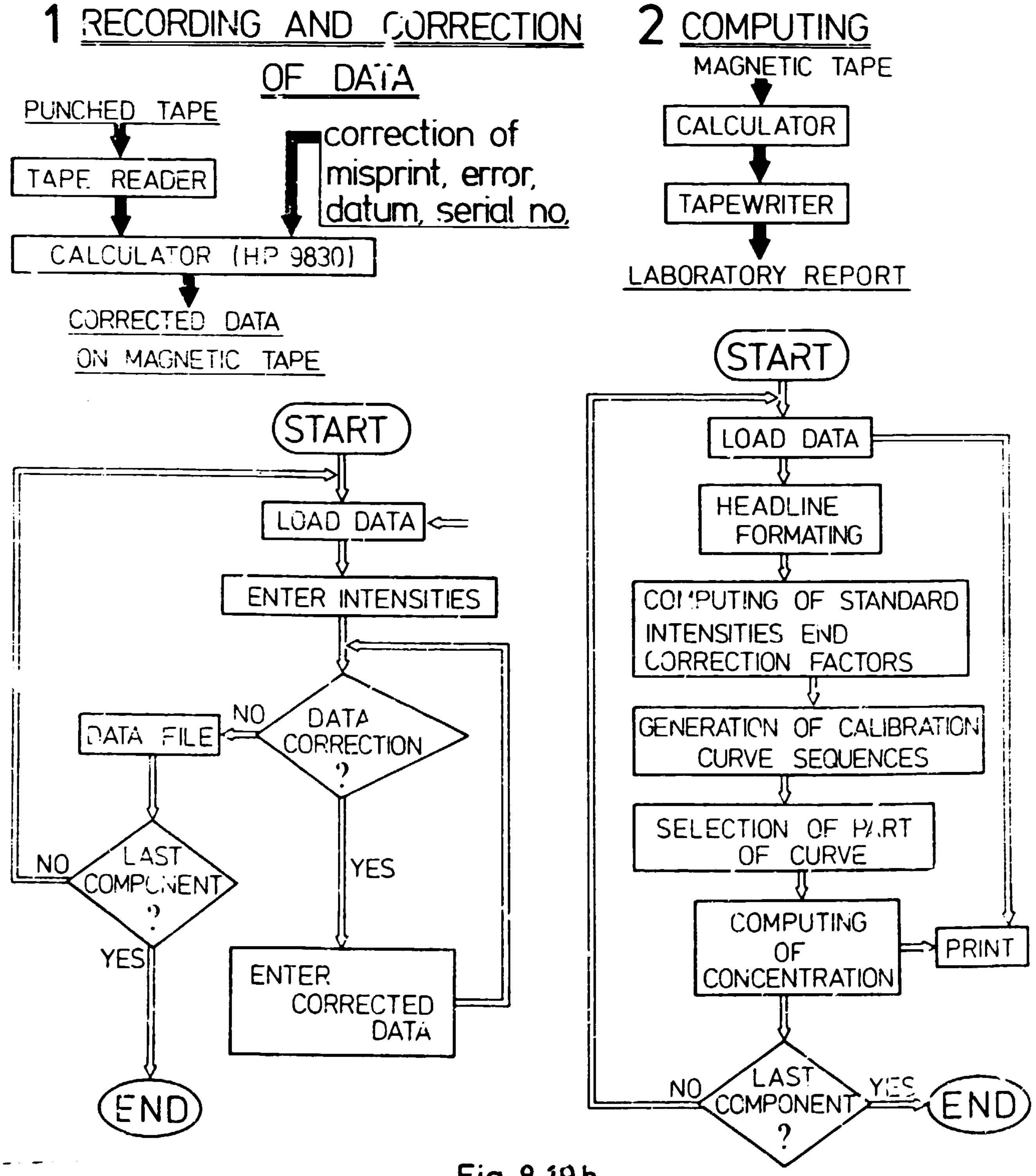


Fig. 8.19b
DATA PROCESSING

TIME CONSUMPTION

6 hours/6 samples for all components.

FLAME PHOTOMETRIC DETERMINATION OF SODIUM CONTENT OF RED MUD

This procedure can be applied as a part of the AAS analytical system for the determination of main components of red mud and bauxite samples but it is generally used as an independent method from practical point of wiev.

PRINCIPLE

The sodium content of red mud can be extracted with diluted mineral acid at boiling temperature. After sedimentation the solution containing the sodium content can be diluted to the suitable sodium concentration and can be determined with flame photometer. In this case the determination is performed with a Pye-Unicam SP 1900 AAS instrument in emission mode.

PROCEDURE

Sample Preparation

Weigh in 0.5 g of 12 different air-dry red mud samples as well as one standard red mud sample with known sodium content and transfer them to 250 ml beakers. Swirl the solid material with 50 ml of distilled water, add 2.5 ml of 20 % ammonium nitrate and 2.5 ml of 1.1 diluted nitric acid. Heat the mixture till boiling and continue for 30 minutes. Set the pH of the hot solution to 7-8 with 1.1 diluted ammonium hydroxide (about 3 ml), add three drops of 30 % hydrogen peroxide and boil for another three minutes. Let it cool and pour to 250 ml volumetric flask. Fill up to the mark with distilled water and take a suitable aliquot (generally five ml) to 100 ml volumetric flask after sedimentation. Fill up to the mark with double distilled water and measure the sodium content according to the next paragraph.

Flame Photometric Measurement

A Pye Unicam SP 1900 can be used in emission mode. Some items of installation of this instrument can be read in the previous part included in the AAS determination of mean components. Adjust the wavelength scale of the instrument to the appropriate setting for the sodium D line, 589 nm. Place the 100 ppm sodium solution in the aspirator and open the slit to the 150 position. Ignite the acetylene-air flame and adjust the wavelength control to maximum response aspirating the 100 ppm sodium solution. Set the sensitivity or scale expansion control knob to give 600 reading on the display for the standard solution. For zeroing use double distilled water as blank. Select the 4 sec integration period and measure the sodium light intensity aspirating all the sample solutions. Control the intensity of standard solution about each fifth sample.

CALCULATIONS

A Texas SR 52 programable pocket calculator is used for the evaluation of sodium content of samples. The moisture corrected equation and the calibration curve from 2.5 ppm to 15 ppm sodium solution are fed to the program card previously. Feed the weight, moisture and intensity data of the red mud samples using the required data file knob and read the sodium oxide content in percent units.

PRECISION

Variation coefficient is 1.

TIME CONSUMPTION

4 hours/12 sample.

11. DETERMINATION OF THE PORE SIZE DISTRIBUTION WITH MERCURY PRESSURE POROSIMETER

The instrument is suitable to determine the pore volume and pore size distribution of bauxites, aluminas and red muds. (See Theory, Volume 5.)

DETERMINATION OF MACRO-PORE SIZE DISTRIBUTION

ANALYSIS PROCEDURE

Sample prepaparation

Before the analysis the sample has to be cleaned from pollutants, which have a disturbing effect on the measure, by degassing in vacuum.

Detailed outline of the sample preparation is the following:

1. Dry the sample in a drying oven
2. Clean and dry the dilatometer and its removable stem
3. Weight the sample into the sample holder of the dilatometer. The quantity of the sample should be chosen considering the expected total pore volume
4. Lubricate in thin layer the ground part and the end of the capillary cone with vacuum grease
5. Seal up the dilatometer with its stem and place into the filling device
6. Shut off all three valves (marked M, A, P) of the filling device
7. Close the aerating stopcock of the glass header connected with the filling device and open its bypass stopcock
8. Set going the vacuum pump

9. Carefully open the P valve of the filling device, taking care that the air flow does not take away the powder
10. After completely opening the valve the material is evacuated till 2.10^{-2} torr. The period of the sample degassing is two hours
11. After the degassing period, slowly open the M valve and fill the dilatometer with mercury. Take care that the P valve should be opened. When the mercury reaches the capillary, close the M valve at every cc. 20 mm level increase. With patting the dilatometer promote the mercury penetration into the pores and grain interpaces.

Hereby the sample preparation has been finished, the sample is ready for measuring.

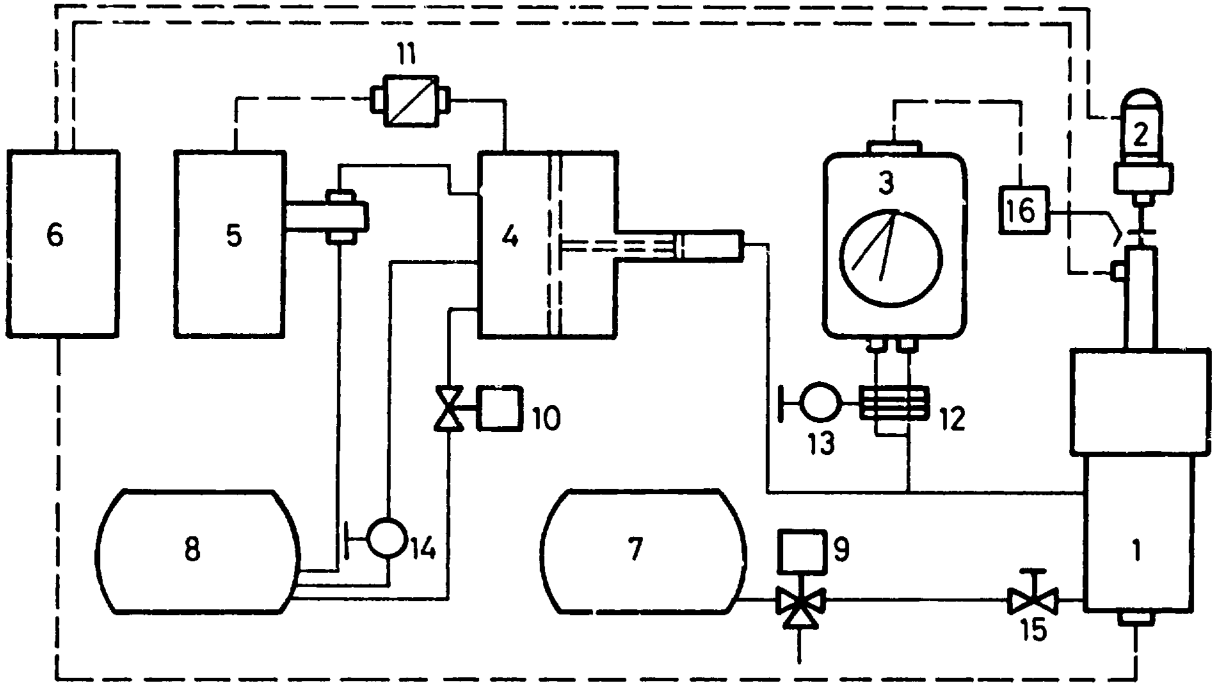
Description of the Instrument

In the course of this laboratory practice, a high pressure mercury porosimeter, Type 70H is used. With it the pore size distribution can be determined in the range of 4-38000 nm (with the filling device).

The pores with size higher than 7500 nm can be determined with the aid of the filling device of the instrument. The measuring device itself - in which the analysis of the pores with radii smaller than 7500 nm is carried out - consists of a small autoclave containing the dilatometer. The mercury present in the calibrated stem of the dilatometer makes contact with a rod, supplied to following the mercury level. Its advancement is controlled by a synchronous motor. The mercury level is followed electrically by means of an electronic relay which operates only with a metallic contact. When a pressure increase causes a lowering of the mercury level in the calibrated stem and the rod does not make contact with the mercury any more, the motor starts and re-establishes the rod-mercury contact. At the same time the mercury level change is recorded by the chart redorder. The pressure necessary to press the mercury into the pores is produced in the pressure multiplier circuit (Fig.8.20). As a result of the analysis the pressure of the system as a function of mercury level is obtained, from which the pore size distribution (see Theory, Vol.5.) can be calculated.

Detailed description of the analysis procedure

1. Read the height of the mercury level in the capillary of the dilatometer, containing the sample. This is performed with the aid of a cathetometer, taking care of its horizontality. Read the pressure on the manometer.
2. Close the bypass stopcock of the glass header. Switch off the vacuum pump and aerate it with opening the aerating stopcock. After this the stopcock should be opened
3. With the aid of the bypass stopcock, increase the pressure with approx. 150 torr and after patting the dilatometer read the pressure on manometer, and the mercury level charge by cathetometer. This is repeated until the pressure on the manometer reaches zero value. The last measuring is made on atmospheric pressure.
4. Bring the mercury level advencement neddle in the autoclave head of the porosimeter in its upper position till the red index under the plate of the bayonet joint is seen.
5. Control the rubber seals. In case of changing them, luricate with grease in thin layer.
6. Make sure that in the bottom of the autoclave there is a drop of mercury.
7. Take off the dilatometer from the filling device, wipe the grease from its upper end and place it into the autoclave with the aid of a wire crook.



1. AUTOCLAVE
2. ROD ADVANCEMENT MOTOR
3. RECORDER
4. PRESSURE MULTIPLIER CYLINDER
5. LOW PRESSURE PUMP
6. MOTOR OPERATION CIRCUIT
7. ALCOHOL RESERVOIR
8. OIL RESERVOIR
9. ALCOHOL DISCHARGE SOLENOID VALVE
10. OIL DISCHARGE SOLENOID VALVE
11. PRESSURE GAUGE
12. SHUT OFF AUTOMATIC VALVE
13. HIGH PRESSURE SAFETY VALVE
14. LOW PRESSURE SAFETY VALVE
15. HIGH PRESSURE MANUAL VALVE
16. CHART ADVENCEMENT DEVICE

Fig. 8.20

SCHEMATIC DIAGRAM OF THE POROSIMETER

8. Fill with abs. alcohol that part of the capillary which is free from mercury.

9. Mount the head of the autoclave and fix it with the nut bolt. Screw it gently by hands only.

10. Screw in the small alcohol overflow valve to half way.

11. Put paper into the recorder chart, adjust the paper chart to zero, and mark the starting point.

12. Connect the autoclave head to the rod advancement motor with the bayonet joint. Connect the advancement motor shaft with the rod.

13. Make sure that the aerating valve is closed. If it is not, close it.

14. Adjust the signal disc of the low pressure circuit to 20.5 atm.

15. Turn on the MAIN switch.

16. Switch the "LEVEL B_3" to the lower position. The rod advancement motor begins to move until reaching the mercury level in the stem of the dilatometer.

17. After running down of the motor, turn the switch "RECORDER B_2" to the position "ON".

18. Open the alcohol discharge valve and fill the autoclave with alcohol. When the alcohol flows through the overflow valve, close it so that no air bubbles would form in it. After this close the alcohol discharge valve, too.

19. Press the PUMP B_1 button. The measure is started. Now the analysis goes on automatically.

20. The analysis procedure is finished, when the blue pen of the high pressure recorder reaches 2000 atm. Than stop the pump with the PUMB B_1 button.

21. Switch the LEVEL B_3 to the upper position and with the aid of the aerating valve decrease the pressure in the autoclave gradually till atmospheric pressure.

22. After reaching the atmospheric pressure, discharge the oil from the cylinder with turning on the OIL V_2-switch. The piston gradually sinks and when the rod indicating its position shows the bottom dead centre, stop the process by turning off the switch.

23. Discharge the alcohol from the autoclave with turning on the ALCOHOL V_1 switch. Open the alcohol discharge-, then the alcohol overflow valves and wait until the alcohol flows out through a tube at the right side of the instrument. After discharging the alcohol, close the alcohol discharge valve and turn the ALCOHOL V_1 switch off.

24. Close the aerating valve.

25. Turn off the RECORDER V_1 swithch.

26. Replace the shaft-contact to the screw on the front panel of the instrument.

27. Unscrew the bayonet joint of the driving shaft.

28. Screw out the alcohol overflow valve.

29. Turn off the MAIN switch.

30. Unscrew fixing nut of the autoclave head and take off the head.

31. Take off the dilatometer.

32. Extract the paper chart from the recorder.

CALCULATION OF PORE SIZE DISTRIBUTION

The calculation is carried out with the aid of a data sheet.

1. In the first step the pressure exerted on the material, and the decrease of mercury level caused by the pressure are calculated. (p_{atm} (1) and mercury level lowering (mm) (2) columns on the sheet).

a) Macropore region

This region ranges from 0 to 760 Hgmm pressure. (Values determined by the filling device)

- The manometer is read off at 0.02 torr, corresponding to zero manometer position. Subract from this value the subsequently measured reduced pressure values. In this way the pressure exerted on the mercury level is obtained.
- Decreases of the mercury level related to the starting value can be determined subtracting the mercury level measured at individual pressures by the cathetometer from the starting value (2nd column). The height of mercury level in the dilatometer filled up to mark is 150 mm. Subtracting the decreases of mercury level from this, gives the pressure of mercury column in the capillary.
- The pressure exerted on the mercury level and the pressure of the mercury column in the dilatometer affect together the material in the bottom of the dilatometer so this two values have to be summed up. So the pressure exerted on the material is obtained in torrs. This value is calculated for atm units by dividing with 760 (1st column).

b) Meso- and micropore region

- The mercury level decreses at various pressures (cc. 2, 6, 12, 20, 30, 40, 50, 60, 80, 100, 150, 200, 250, 300, 400, 600, 800, 1200, 1600, 1800, 2000) are determined from the graph. The pressures are described in the first, the mercury level decreases in the second column. Take care when reading the red, low pressure curve off that its values have to be corrected with the difference of the deviation from zero at the starting.

2. Determination of the mercury level decrease corrected by the mercury compressibility (3rd column); of the total corrected mercury level decrease (4th column) and of the mercury column height (5th column).

- Correcting the mercury level decrease read off the graph, by the mercury compressibility gives the decrease of the mercury level caused by the mercury penetration into the pores. The mercury compressibility in function of the pressure can be determined with the aid of a calibration curve. The obtained data have to be written into the third column of the data sheet.
- For determining the total mercury level decrease (4 column) add together the last measured and corrected mercury level decrease in the macropore region, and the individual corrected mercury level decreases in the meso- and micropore region, respectively.
- The height of the mercury column (5th column) is obtained by subtracting the total corrected mercury level decreases determined for the individual pressure from the value of the greatest total corrected mercury level decrease.

3. Calculation of the pore radius (R, 6th column) and the pore volume (V, 7th column).

- The value of the pore radius is determined based on the following equation:

$$R = \frac{7500}{p}$$

where:

R : pore radius in nm

p : pressure in atm

In the meso- and micropore region 1 atm has to be added to the pressure values read off the graph, because the pressure gauge of the instrument records overpressure. The calculated values are tabulated in the 6th column of the data sheet.

- The pore volume is calculated by the following equation:

$$V = \frac{A \cdot H}{Q}$$

where:

H : height of the mercury column, mm

A : cross-section of the dilatometer
$A = 7.067\ \mathrm{mm}^2$

Q : weight of the sample used

V : pore volume in mm^3/g

The graph of the pore volumes plotted in the function of their radii gives the integral pore distribution curve of the sample. The most probable pore radii values can be determined by its differentation.

In the course of this laboratory practice, the calculations are performed with the aid of the 7th program of the Texas-52 calculator.

Instructions for use of the program are the following:

1. Read the side "A" and "B" of the prerecorded magnetic card according to the instructions in chapter 11. (Calculation of the pore radius and the pore volume).

2. After pressing the key "A":
In the macropore region:

pressure read off the manometer - RUN - mercury level - RUN - p calculated (on the display)

- RUN - calculated decrease of level (on the display)

When calculating the last point in the macropore region the key RUN has to be pressed as soon as the decrease of the mercury level is displayed.

3. After pressing the key "B":

Q value - RUN - the last pressure value in the micropore region - RUN - related mercury level decrease
- RUN - the data of the data sheet in due course.

After each displayed data, press the key RUN.

4. After pressing the key "C":

The data of the macropore region have to be given in the order the data sheet.

After each displayed data, press the key RUN.

5. After pressing the key "D":

values of individual pressures in the micro- and mesopore regions, respectively - RUN - values of the mercury level decreases read off the graph

- RUN - Valves of the data sheet in due course
After each displayed data, press the key RUN

12. CAUSTICIZATION TESTS

PURPOSE OF THE CAUSTICIZATION TEST

Taking into account that the composition, crystal-structure and, consequently, the causticizability of sodium-aluminium-silicates formed during the Bayer process depend significantly on the contaminants of the digestion liquor (Cl^-, CO_3^{--}, SO_4^{--}, etc.) and on the digestion parameters (see notes in Volume 6), it is expedient to perform the causticization test always with the given red mud, in order to establish optimum causticization technology.

Red mud samples freshly prepared or freshly taken from the plant are used for the causticization tests, as their causticizability is considerably affected by the aging of sodium-silicates.

TESTING EQUIPMENT

Causticization tests are performed in a closed vessel of 1 to 2 l volume placed into water bath, equipped with closing lid and agitator. The vessel can be thermostated at 90 to 100 °C.

RUNNING THE TEST

Mud from the last washer underflow of the (Almásfüzitő Alumina) plant is used for the red mud causticization tests, with known solids content and Na_2O total, Na_2O_c and Al_2O_3 concentrations of the liquid phase.

Solids content of the red mud slurry to be causticized is adjusted to 250 gpl by a liquor of similar concentration, and 4 times 700 ml slurry is measured into 4 beakers of 1 litre volume each. Finally, ground CaO is added to the red mud doses, calculated in the amount of 1, 2, 3 and 4 mol CaO to its bound Na_2O content, by the following formula:

$$CaO_{\underline{\sigma}} = nx\ 0.7 \times 2.5\ Na_2O \times \frac{56}{62}$$

where:

n : number of CaO mols (1, 2, 3 or 4) calculated for the bound Na_2O content

Na_2O : bound Na_2O content of red mud in percentages

After adding CaO to the slurry, it is thoroughly stirred with a glass rod and filled into preheated vessels of 95 °C temperature, placed in thermostated water bath. The vessels are closed and the stirrer is started. Stirring is carried out on 95 °C temperature, for 4 hours. Of the test performed by 3 mol CaO charge, the slurry samples are taken after 1, 2, 3 and 4 hours; of the other tests the samples are taken after 4 hours, 100-100 ml in each case. Solids content of the slurry samples are separated by centrifuge, then it is repulped, washed 3 times by 400 to 500 ml of distilled hot water.

The washed red mud samples are dried on 110 °C temperature, then ground to <100 /um grain size for the analysis.

The following components of the red mud samples are analysed by atomic adsorption spectrometry method:

Fe_2O_3,
SiO_2 ,
CaO ,
Na_2O

EVALUATION OF CAUSTICIZATION TEST

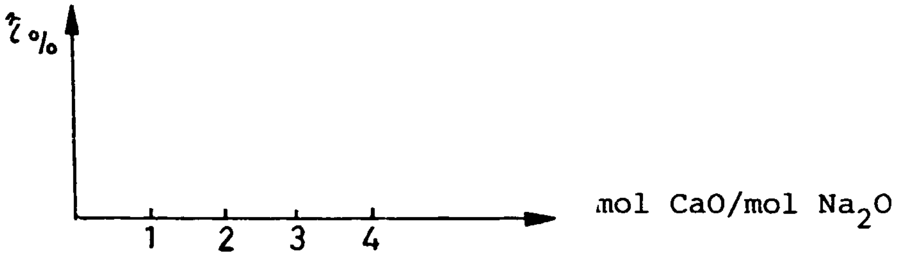
1. Calculate for each tested sample the causticization efficiency, according to the following formula:

$$\eta_{caust.} = (1 - \frac{a \cdot b'}{a' \cdot b}) \cdot 100 \quad \text{per cent}$$

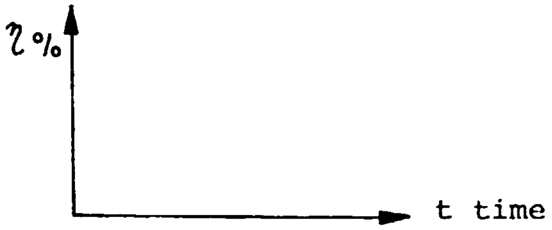
where:

a : Na_2O content of causticized red mud, in percentage
b : Fe_2O_3 content of causticized red mud, in percentage
a' : Na_2O content of the initial red mud, in percentage
b' : Fe_2O_3 content of the initial red mud, in percentage

2. Plot the causticization efficiency in the function of the applied CaO amount.



3. In the test performed by 3 mols of CaO/mol Na_2O, plot into the diagram the shaping of causticization efficiency, in the function of the reaction time.



4. Calculate the amount of CaO mols for 1 mol of regenerated Na_2O, in case of red mud causticized by additin of 1, 2, 3 and 4 mol CaO and 4 hours reaction time, using the following formula:

$$n' = \frac{100 \cdot c}{a' \cdot \eta} \cdot \frac{62}{56}$$

where:

c : CaO content of causticized red mud, per cent
a' : Na_2O content of initial red mud, per cent

13. ANALYSIS OF ALUMINATE LIQUOR

CONDUCTIVITY MEASUREMENT OF ALUMINATE LIQUORS

INTRODUCTION

A substantial requirement of process control is that the caustic soda concentration (c_k), the alumina concentration (c_a), the temporary caustic molar ratio (α) as well as the salt level (c_s) of the process liquor has to be known permanently. Thermometric and conductometric concentration measurement methods were developed for this purpose (exercise 21.), as well.

Changing of conductivity of aluminate liquors in function of Na_2O_{caust} concentration at different salt levels is shown in Fig.8.21 at different Al_2O_3 concentrations in Fig.8.22 at different caustic molar ratios in Fig.8.23.

The conductivity of the liquor depends considerably on the temperature of the solution - 1 pct per ^{o}C on the average - Fig.8.24.

It is seen in Fig.8.23 that the conductivity is independent of the salt content (c_s) of the solution at 50 gpl Na_2O_{caust}, so the measurement will be carried out with liquors diluted to 50 gpl.

INSTRUMENTATION

Measurement is carried out with an OSCIMHOMETER equipment of OK-105 type. The characteristic data of the instrument are given in Table 8.8.

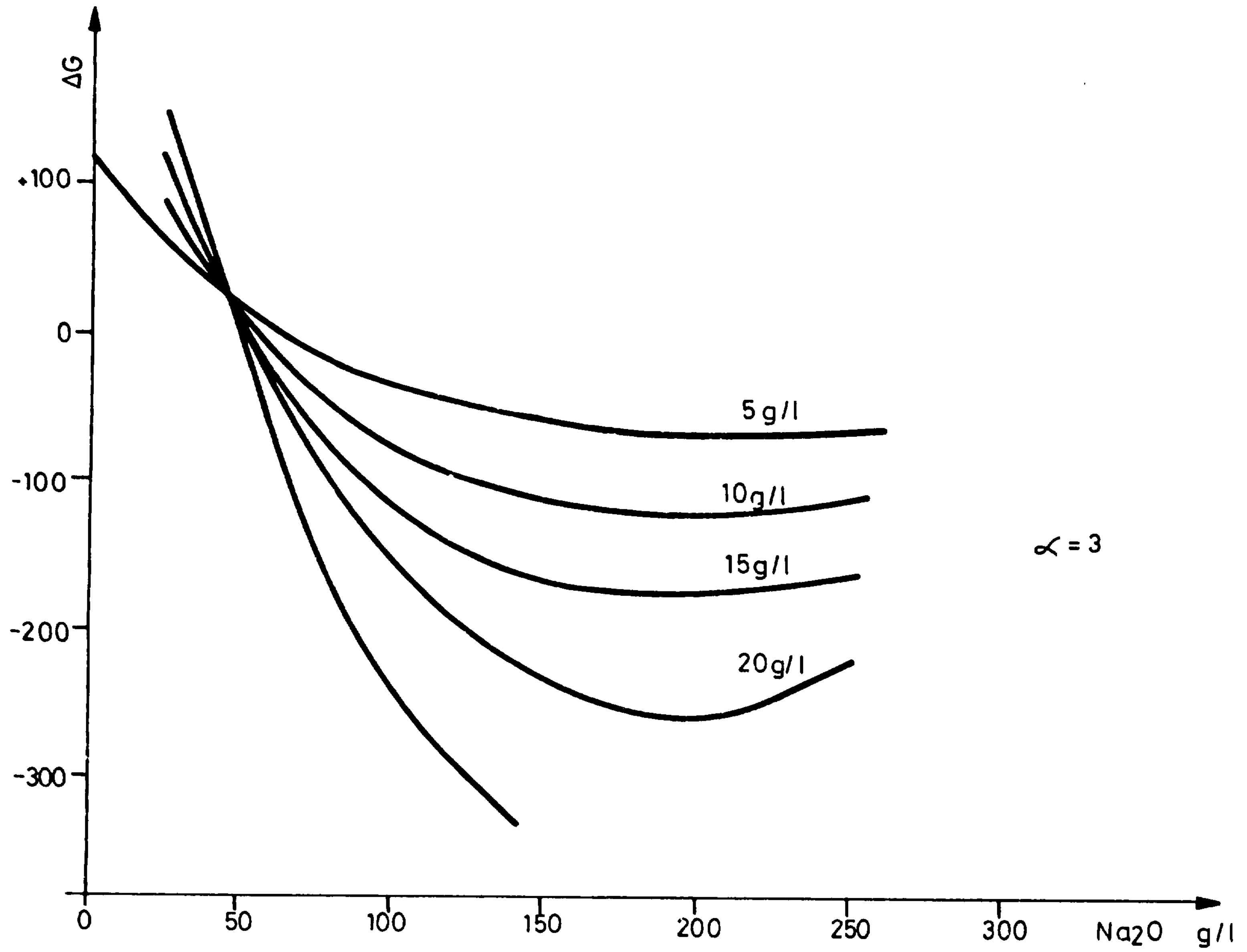


Fig. 8.21

CONDUCTIVITY vs. SALT LEVEL AND CAUSTIC CONCENTRATION

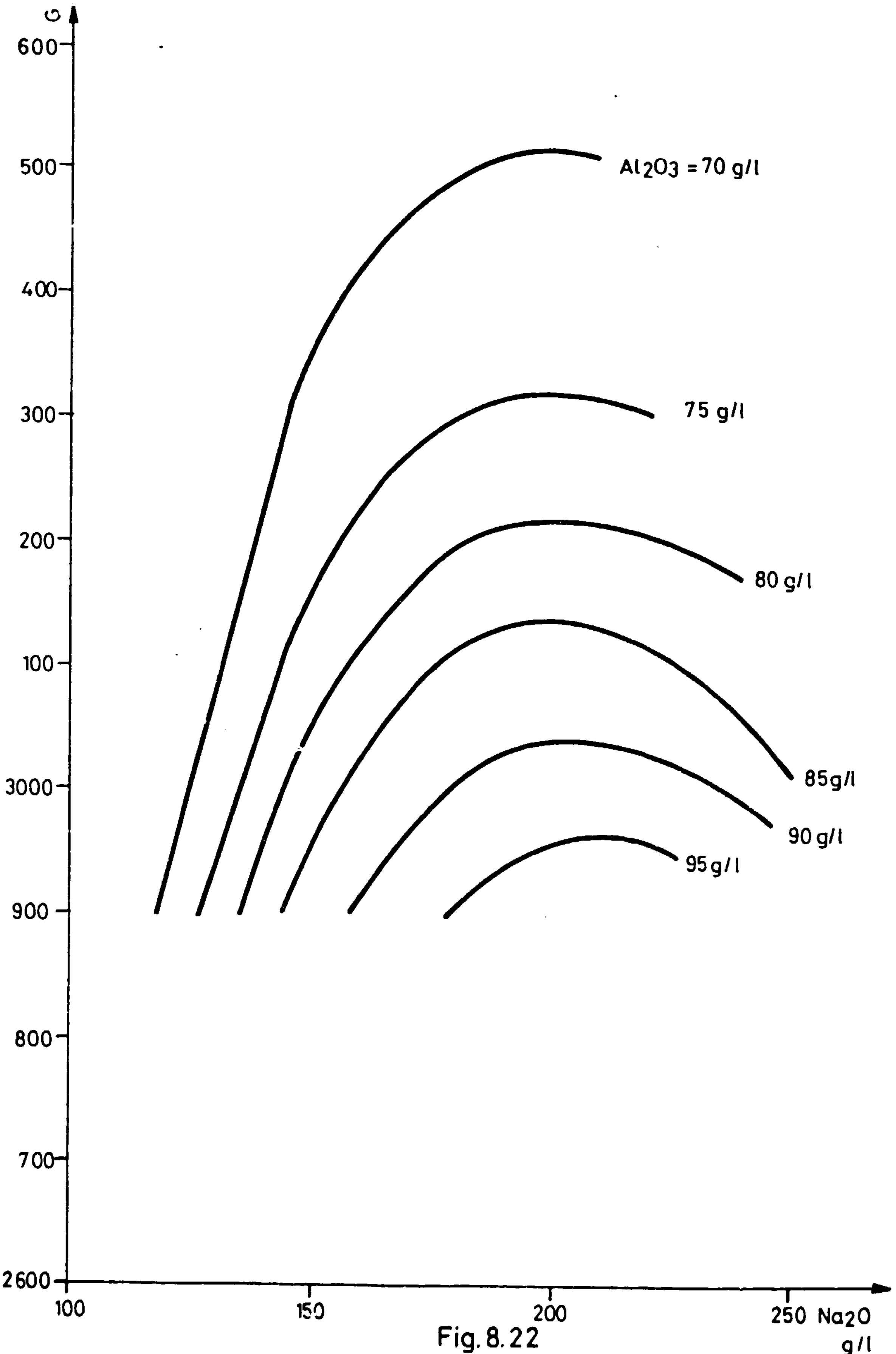


Fig. 8.22
CONDUCTIVITY vs. Al_2O_3 AND Na_2O CONCENTRATION OF THE LIQUOR

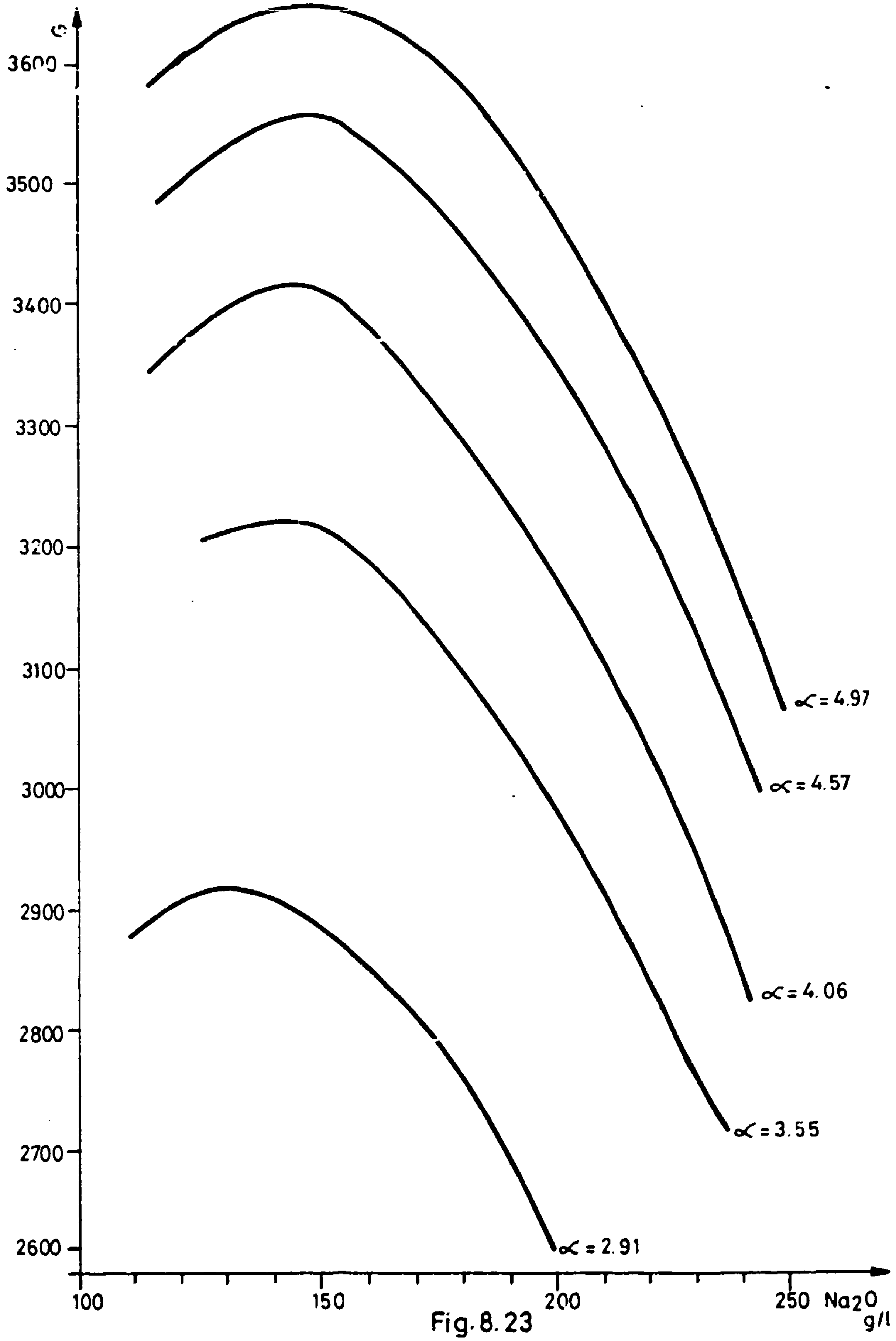


Fig. 8.23

CONDUCTIVITY vs. MOLAR RATIO AND CAUSTIC CONCENTRATION

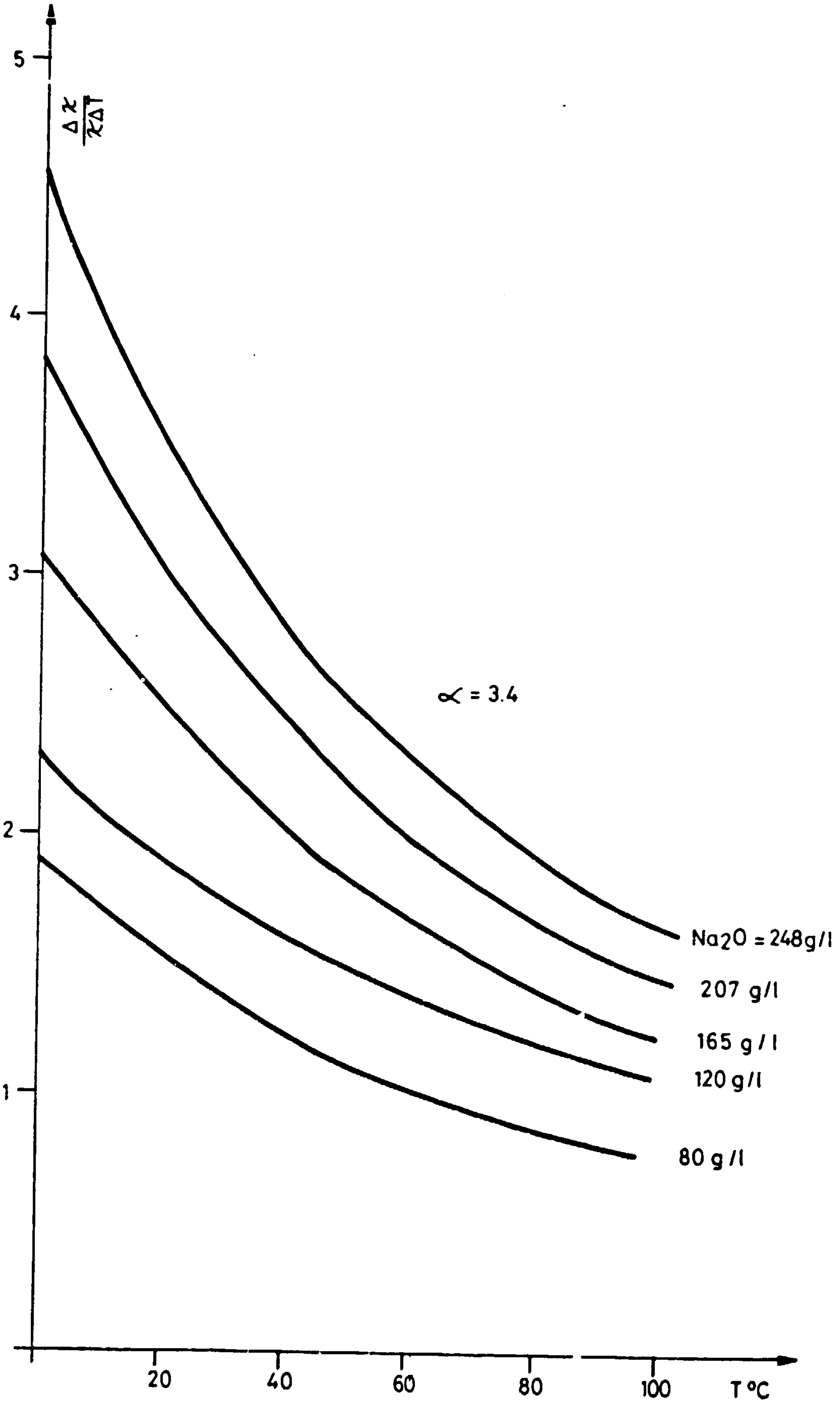


Fig. 8.24

CONDUCTIVITY vs. TEMPERATURE OF LIQUOR

Table 8.8

TECHNICAL DATA OF OSCIMCHOMETER

Measuring range:	1x10^{-6}-50 Mho.cm^{-1}, depending on type of the applied cell
Measuring frequency:	4MHz
Measuring accuracy:	± 0.5 rel. %
Measuring sensitivity:	appr. 0.2 %
Stability (without diameter compensation):	the observed values are reproducible with a ± 0.5 % accuracy, if the temperature is between +15 - +35°C and the main voltage fluctuation is not more than ± 10 %.
Decreasing the error, caused by the changes of the cell diameter in the case of prescribed setting in of the diameter-compensation:	Depending from the changes of diameter and electric conductivity of the solution can be two to hundredfold
The diameter-compensation can be used:	between the values of RANGE 0 - 3000
Mains supply:	220 V/50 Hz
Power consumption:	appr. 15 W
Dimensions:	280 x 200 x 180 mm
Weight:	appr. 6.5 kg
Measuring cells:	1 measuring coil, 1-1 400 ml universal measuring cell beakertype cell and transflux glass-cell, made of glass. Other cell-types can be also used with or made for the instrument.

Measurements will be done under isotherm conditions, namely at 50 °C, so the measuring cell is to be thermostated.

MEASURING

Prepare solutions of $\alpha_1 = 1.5$ (A/C = 0.642), $\alpha_2 = 1.8(0.535)$, $\alpha_3 = 2.1(0.458)$, $\alpha_4 = 2.4(0.401)$, $\alpha_5 = 2.7(0.356)$, $\alpha_6 = 3.0(0.321)$ using the plant liquors of $\alpha = 1.5(0.642)$ and 3.0(0.321).
Dilute them to 50 Na_2O_c gpl (85.5 Na_2CO_{3c} gpl) for the measuring.

Measure the conductivities of the 6 solutions 5 to,es each, and prepare calibration curves.

RESULTS

Calculate the arithmetical mean at each point, and calculate the actual deviation as well.

Plot the conductivity values in fuction of caustic molar ratio and in function of A/C ratio. Put it away as a calibration curve to the exercise 14.

DETERMINATION OF Ga CONTENT OF ALUMINATE LIQUOR BY PULSE POLAROGRAPHIC METHOD

PRINCIPLE

The gallium forms weak thiocianate complex which can be reduced on mercury working electrode and the polarographic wave can be recorded in case of properly selected conditions. Main determinating factors are the ionic strength and the pH. The application of a pulse polarograph suitable for its better selectivity and sensitivity.

PROCEDURE

Dilute an aluminate sample to 1:5 volume fraction with distilled water and pipet 10.0 ml of this solution to a 50 ml baker. Add 5 ml cc nitric acid and evaporate to 0.5 ml volume. Treat it with small portion of 4-5 ml of 30 % hydrogen peroxide till the colour of the precipitate becomes white. Evaporate to dry and dissolved the residue with 1 ml of cc nitric acid and water. Evaporate the solution two times to 1/3 volume to decrease the acidity. Add 20.0 ml of 7.5 F $NaClO_4$ and 3.0 ml of 2 F NaSCN and set the pH of the solution to 0-1.5. Poure the solution to the polarographic cell and pourge with nitrogene to eliminate the oxigen content of the solution.

Know the operation and structure of the Tacussel UAP 4 pulse polarograph from the instrument's manual. Set the measuring parameters according to the next data:

Start potantial:	- 0.6 V vs S.C.E.
End potantial:	- 0.1 V vs S.C.E.
Drop life time:	1.5 sec
Delay time:	1.3 sec
Duration:	40 msec
Puls amplitude:	40 mV
Polarisation rate:	0.4 mV/sec

Take the polarogram of sample solution, add 0.10 ml of standard Ga solution and repeat the procedure.

CALCULATION

Measure the peak height of sample and sample + addition peaks and calculate the gallium content with the following equation:

$$\text{Ga}, \text{g/l} = \frac{H_S \cdot C_A}{H_{S+A} - H_S} \cdot 10$$

where H_S sample peak height
H_{S+A} sample + addition peak height
C_A Ga concentration of standard solution (mg/ml)

Precision

Variation coefficient is 5.

Time consumption

30 min.

14. $Al/OH/_3$ PRECIPITATION AND ANALYSIS OF LIQUID PHASE

$Al/OH/_3$ PRECIPITATION

Application fields and difficulties of precipitation model tests are described in Chapter 3. of Volume 6. Some of the most frequent application fields are enumerated hereunder:

- effect of precipitation parameters - as initial molar ratio, Na_2O_C concentration, precipitation time, initial temperature run-down, seeding ratio, grain size distribution of seed - on efficiency and on grain-size distribution of the product
- activity determination of seed crystal
- effect of the aluminate liquor contaminants - CO_3; C_{org}; oxalate, Fe_2O_3, SiO_2 content - on the precipitation.

LABORATORY PRECIPITATION EQUIPMENTS

Precipitation model experiments are carried out according to Volume 6 chapter 3., using the most suitable equipment as regards the purpose of the test.

In case of tests which are very sensitive as regards precipitation such as the modelling of agglomeration, precipitation bombs are used. Digestion bombs illustrated in the exercise No. 8 (Fig. 8.12) are also suitable for precipitation purposes. The bombs are agitated in the thermostated agitating unit with 17 rev./min. In certain cases iron dissolution from the wall of the bomb greater by order of magnitude than that of the plant must be prevented as a consequence of the difference of the tank wall surface per unit precipitator volume. In this case the precipitator bomb is line with titanium nickel or teflon.

If the plant precipitation to be modelled is performed in a mechanically agitated equipment, a similar laboratory unit must be used (Fig. 8.25). Care must be taken for the type of the stirrer and for selecting the applied revolution number, so that the shear velocities affecting the grain be the same as that in the plant equipment.

A more up-to-date equipment is a laboratory air-agitation unit (Fig. 8.26), where the agitation is provided by air blown into the draft tube, consequently the hydrate grains are exposed to smaller shear forces. When shaping the unit, care must be taken that the total amount of slurry be mixed. Flow velocity corresponding to that of the plant can be adjusted by the pressure of compressed air. The specific air consumption is much higher than that of the plant, due to the difference in the pressure conditions. As a consequence of intensive contact with the air, much greater evaporation is experienced than in the mechanic equipment, therefore, continuous substitution of evaporated water has to be ensured.

Due to the fact described under Volume 6. chapter 3. the precipitation tests are often performed under isotherm conditions. In such cases maintaining ± 0.5 °C temperature is sufficient. In case of performing longer precipitation tests, heat control program corresponding to the plant temperature-regime has to be ensured. A simple, natural (logarythmic) temperature control program, suiting the cooling profile is used for realization of the exercise (Fig. 8.27).

PERFORMING THE MEASUREMENT

Evaluations are carried out in the unit shown in Fig. 8.25. Main data of the unit are given hereunder:

Number of precipitation vessels:	6 pcs.
Effective volume of precipitation vessels:	600 ml

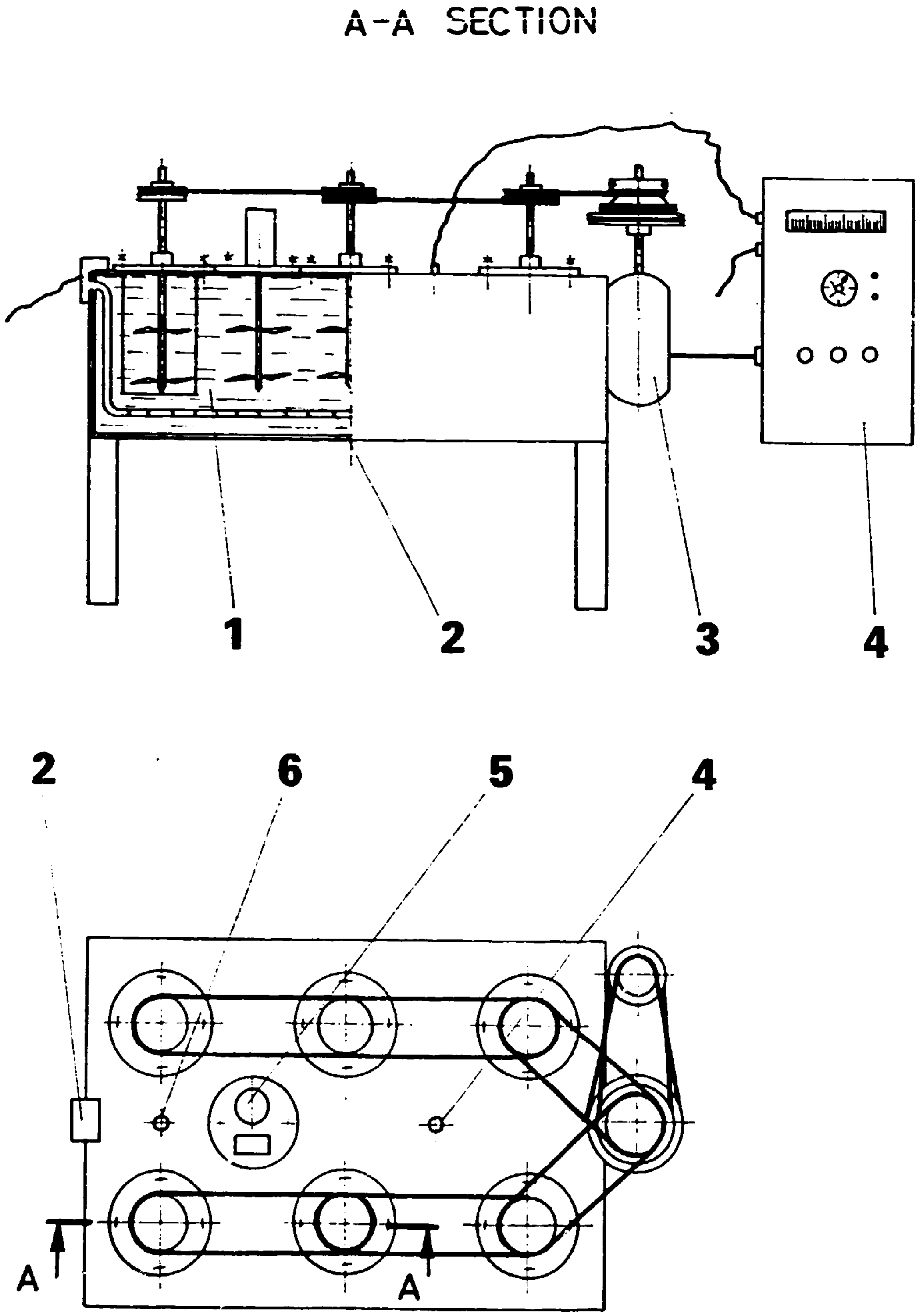


Fig. 8.25

MECHANICAL LABORATORY PRECIPITATOR

1 Oil
2 Heating element
3 Motor
4 Thermostat
5 Stirrer
6 Thermometer

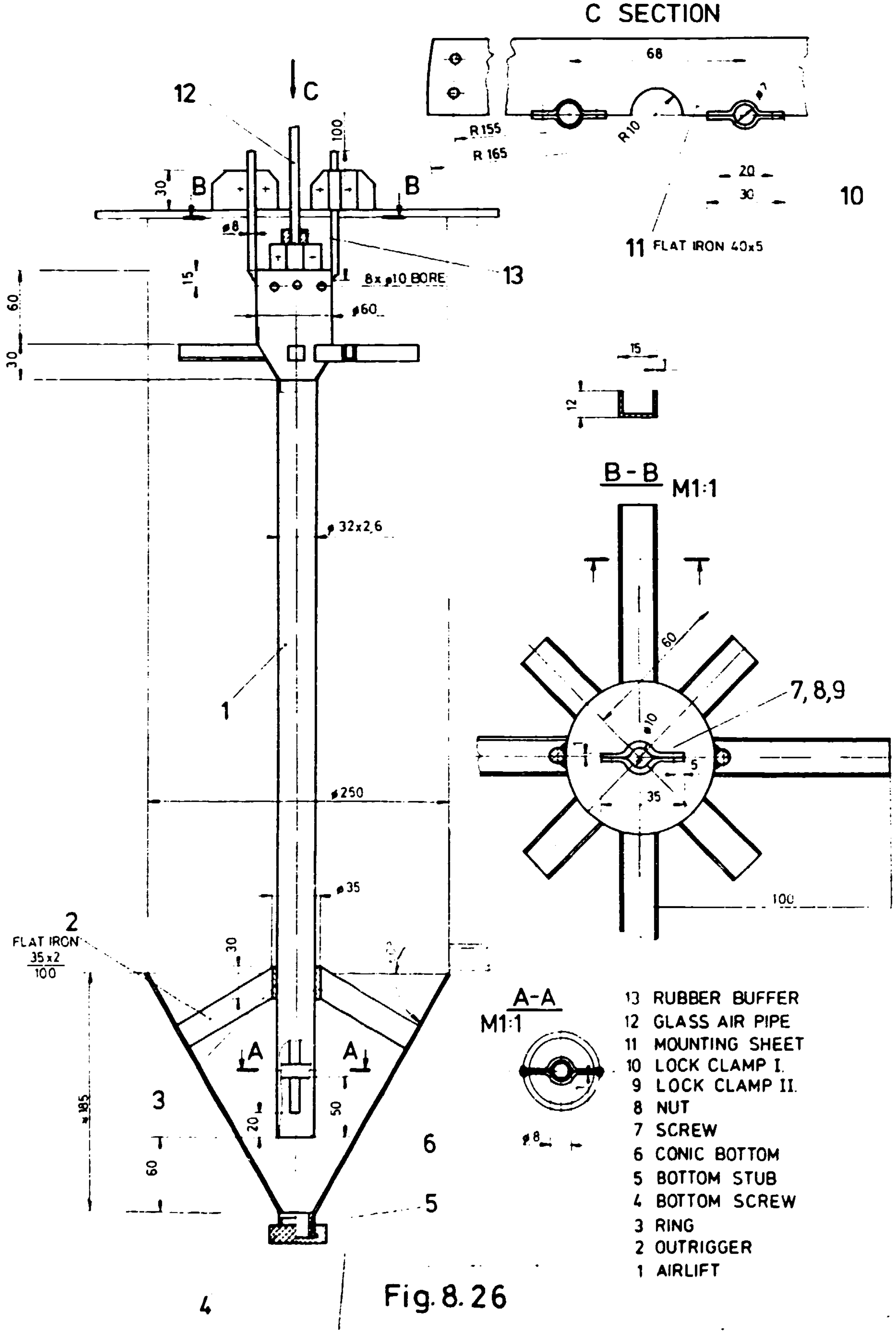


Fig. 8.26

LABORATORY AIRPRECIPITATOR TANK

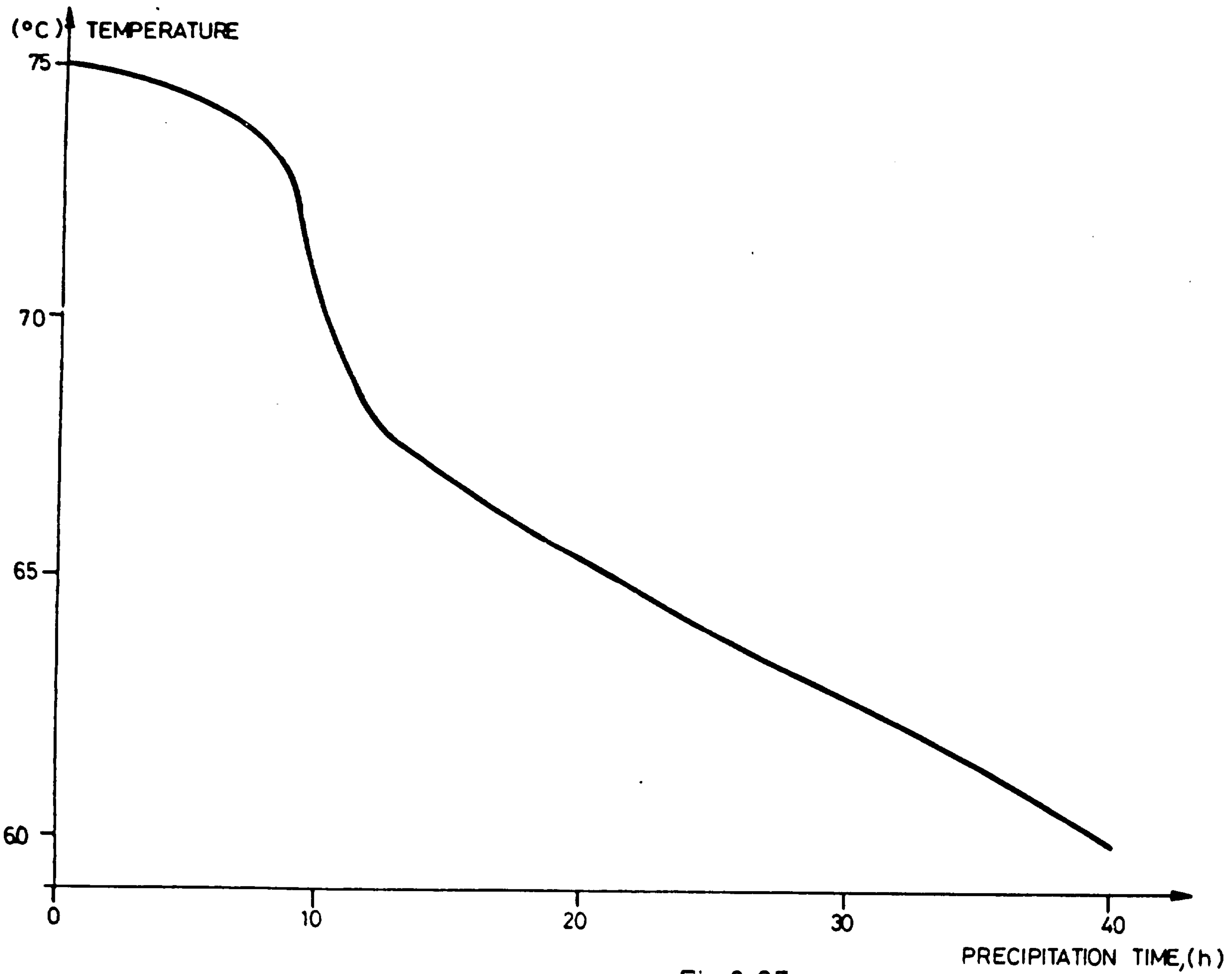


Fig.8.27
COOLING PROFILE FOR PRECIPITATION TESTS

Revolution number of the engine: 1390 r/min
Revolution number of precipitator: 83 r/min
Length of the stirrer: 7 cm

Velocity of separation is followed by the molar ratio determination based on conductivity measurement, as described in exercise No. 13. Grain-size distribution of the product hydrate is determined in the course of exercise 18. and, based on the result, the specific surface area is also calculated.

Required dilutions for the exercises are made of plant liquor of about 1.5 molar ratio (A/C = 0.64) above 200 gpl $Na_2O_{caust.}$ (340 gpl $Na_2CO_{3caust.}$) concentration; or from similar synthetic liquor. The amount of seed hydrate is calculated on the basis of the given seeding ratio as follows:

$$SC = \frac{A_s}{A_1}$$

$A_s = Al_2O_3$ in seed
$A_1 = Al_2O_3$ in aluminate liquor

$$G_s = A_1 \cdot SC \; \frac{156}{102} \cdot \frac{1}{0.87} \cdot \frac{V}{1000} \qquad /g/$$

where: $\frac{156}{102} = \frac{Al/OH/_3}{Al_2O_3}$ molar weight ratio

0.87 = $Al(OH)_3$ content of hydrate containing 13 per cent adh. liquor
V = volume of aluminate liquor, in ml

MEASUREMENT OF CONCENTRATION-DEPENDANCE

- initial temperature: 70 °C
- aluminate liquor concentrations:

600 ccm 90 gpl $Na_2O_c \sim$ 160 gpl Na_2CO_{3c}
600 ccm 110 gpl $Na_2O_c \sim$ 190 gpl Na_2CO_{3c}
1800 ccm 130 gpl $Na_2O_c \sim$ 220 gpl Na_2CO_{3c}
600 ccm 150 gpl $Na_2O_c \sim$ 250 gpl Na_2CO_{3c}

- seeding ratio: 1.0
- samples are taken from the liquor of 130 gpl Na_2O_c (220 gpl) content after 1, 2, 3 and 5 hours, and the molar ratio is determined
- samples are taken from each vessels after 20 hours, and the molar ratio is determined. Total amount of hydrate is filtered out, the liquor is washed off by hot, distilled water and then by alcohol, finally the grain-size distribution is determined in the course of exercise No. 18.

SEEDING RATIO DEPENDANCE

- experiments are performed in a liquor of 130 gpl Na_2O_c (220 gpl Na_2CO_{3caust})
- temperature program starts at 70 °C
- successive seeding ratios should be:
  0.5, 1.0, 1.0, 1.0, 1.5, 2.0
- in order to follow the change of efficiency versus time samples are taken from the tank with 1.0 seeding ratios after 1, 2, 3, 5 hours
- after 20 hours samples are taken from each tank for the determination of the molar ratio
- hydrate is treated as described previously.

SODA LEVEL DEPENDANCE

1100 ccm synthetic liquor of 1.0 causticity (free of soda), and 1400 ccm of 0.75 causticity (i.e. 25 per cent soda) is prepared (molar ratio = 1.5 ~ A/C = 0.64; Na_2O_c = 200 gpl $Na_2CO_{3caust.}$ = 340 gpl).

Precipitation of synthetic aluminate liquor

- the calculated amount of Na_2CO_3 is dissolved in hot, distilled water
- the required of NaOH is dissolved during cooling
- the necessary Al-chips are added in small charges, under hood because of intensive H_2-releasing
- solutions of 130 gpl kNa_2O concentration (220 gpl Na_2CO_{3caust}), of 5, 10, 15, 15, 15, 25 per cent soda level (0.95..........0.75 causticity) are prepared from the liquors
- seeding ratio: 1.0
- samples are taken from the liquor of 15 per cent soda level, after of 1, 2, 3, 5 hours, in order to determine the molar ratio
- the product hydrate is treated according to the instructions described under previous point.

SAMPLING

When taking the sample, care must be taken for separating the hydrate grains as quickly as possible and not to let the solution to cool, as it would induce further segregation. Hydrate sample can only be taken from the hydrate gained after filtering the total content of the tank, and care must be taken that the sample be of average quality. After stopping the agitation the hydrate starts to settle immediately, with a velocity corresponding to its size: consequently the slurry sample taken in such case can not be representative as regards grain-size distribution. The hydrate sample has to be washed thoroughly by water and alcohol, because the $Al/OH/_3$ separating from the adh. liquor sticks the grains together.

EVALUATION OF THE RESULTS

EXERCISES

1. plotting the precipitation efficiency vs. time
2. plotting the precipitation efficiency vs. the concentration (1st group), seeding ratio (2nd group) and soda level (3rd group)
3. change in the average grain-size of the product hydrate (fraction below 44 μm), in the function of the above
4. calculation of dispersion, based on three parallelly performed measurements.

CALCULATION OF EFFICIENCY

$$= \frac{A_1 - A_2}{A_2} \cdot 100$$

A_1 = initial Al_2O_3 gpl

A_2 = final Al_2O_3 gpl

In practice it is normed for Na_2O_c or $Na_2CO_{3caust.}$ content to the molar ratio or A/C, resp., because of may be evaporation.

$$\eta = \frac{\frac{A_1}{C_1} - \frac{A_2}{C_2}}{A_1/C_1} \cdot 100 \quad \text{or} \quad \eta = \frac{R_2 - R_1}{R_2}$$

CALCULATION OF DISPERSION

$$\sigma^2 = \sum_{i=1}^{n} \frac{(\bar{x} - x_1)^2}{n} \quad \text{where:} \quad \bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

The results are given in Table 8.9.

Table 8.9

No. of sample	Initial liquor				Precip. time	Precipitated liquor		η prec.	Product dm	-44 μ %
	kNa_2O_c	Na_2CO_{3c}.	R A/C	salt level		molar ratio	A/C			

CHEMICAL ANALYSIS OF ALUMINATE LIQUOR

DETERMINATION OF CAUSTIC SODA CONTENT OF ALUMINATE LIQUOR

Principle

The disturbing anions (CO_3^{2-}, PO_4^{3-}, VO_4^{3-}, F^-) are precipitated with large excess of barium chloride solution. Use an aliquot of clear solution for the titration with hydrochloric acid titrant in the presence of phenolphtalein indicator. The alkalinity originated from sodium-hydroxide and sodium aluminate is measure this way. The disturbing effects of aluminium content can be eliminated with addition of potassium sodium tartarate.

Procedure

Pour about 150 ml water to a 250 ml volumetric flask, add 25 ml of 20 % $BaCl_2$ solution and swirl the content of the flask. Transfer 20 ml of 1.10 diluted aluminate liquor (the dilution depend on the caustic sodium content of the liquor) to the flask with pipet. Fill the flask to the mark with distilled water and close with a ruber stopper tightly. Stirr the mixture shaking the flask frequently. Wait till the precipitate is settled. Transfer 20 ml of Seignette salt solution to a 300 ml Erlenmayer flask and add 0.5 ml of phenolphtalein indicator solution. Pipet an 5 ml aliquot of the settled clear solution to the Erlenmayer flask and titre imediately with 0.1291 F hydrochloric acid titrant till the solution become colourless (V ml).

Calculations

$$Na_2O \text{ caustic } g/l = \frac{(V - 0.06) \cdot 4}{A}$$

where

A : the volume of the original aluminate liquor (calculated from the diluted aliquot)

V : consumed titrant

Precision

Variation coefficient is 0.1.

Time consumption

30 minutes.

DETERMINATION OF Al_2O_3 CONTENT OF ALUMINATE LIQUOR

Principle

The aluminium content of aluminate liquor forms EDTA complex. The excess of a known quantity of EDTA can be titrated back with zinc acetate titrant in the presence of xylenolorange indicator.

Procedure

Transfer 5 ml of diluted aluminate liquor to a 250 ml volumetric flask with pipet and acified with 1:1 HCl till the precipitate is dissolved. Fill the flask to the mark. Pipet 50 ml of this solution to a 200 ml Erlenmayer flask and add 25 ml of 0.12 F EDTA solution with pipet to the flask. Neutralize the solution with 1:1 NH_4OH in the presence of phenolphtalein and add 25 ml of acetate buffer solution of pH 5.5, some boiling stones, cover it with watch glass and boil for 5 minutes. Let the solution cool and titrate with 0.07843 F zinc acetate titrant in the presence of 2-3 drops of 1 % xilenolorange to yellow-violet colour (V).

The titer of the EDTA solution must be determined daily by titration with zinc acetate (V_o).

Calculations

$$Al_2O_3 \text{ content g/l} = \frac{(V_O - V) \cdot 4}{A}$$

where

A : the volume of the original aluminate liquor (calculated from the diluted aliquot) (ml)
V : consumed titrant (ml)
V_O: titrant consumed at blank (ml)

Precision

Variation coefficient is 0.1.

Time consumption

20 minutes

Calculation of caustic molar ratio of aluminate liquor

The most important technological parameter of the aluminate liquor can be calculated from the known Al_2O_3 and caustic sodium content by the following method:

$$\text{Caustic molar ratio} = \frac{Na_2O \text{ g/l}}{Al_2O_3 \text{ g/l}} \cdot 1.645$$

DETERMINATION OF CARBONATE CONTENT OF ALUMINATE LIQUOR

Principle

The $BaCO_3$ content of the precipitate originated from the caustic soda determination can be decomposed with hydrochloric acid. The excess of hydrochloric acid can be titrated back. The Na_2CO_3 content can be calculated from the consumed hydrochloric acid.

Procedure

Filtrate the precipitate remained from the caustic sodium determination on a Buchner funnel and wash four times with 20 ml of 5 % bariumchloride solution. Transfer the precipitate with filter paper to a 300 ml Erlenmayer flask. Give excess of 0.129 F hydrochloric acid (about 20-30 ml) (V_1) with buret and pour 50 ml of distilled water to the flask. Boil it for ten minutes. Titrate the excess of hydrochloric acid with 0.129 F sodium hydroxode solution in the presence of phenolphtalein (V_2). The titration can be performed in hot solution too.

Calculations

$$Na_2O \text{ (soda) } g/l = \frac{V_1 f_1 - V_2 f_2}{5} \cdot C$$

where

V_1 : consumed 0.129 F HCl (ml)
V_2 : consumed 0.129 F NaOH (ml)
f_1 and f_2 : the proper factors
C : constant according to the dilution

$$Na_2CO_3 \, g/l = Na_2O \cdot 1.71 \quad g/l$$

Precision

Variation coefficient is 0.1.

Time consumption

20 minutes

DETERMINATION OF SiO_2 CONTENT OF ALUMINATE LIQUOR

Principle

The silica content of an acidified aluminate liquor forms yellow coloured silica-molybdenic acid which can be reduced with ascorbic acid-Fe^{3+} redoxi system to molybdenic blue and measured spectrophotometrically. The optical density of solution is proportional to the silica content of original sample.

Procedure

Transfer 1 ml of diluted aluminate liquor to a 50 ml volumetric flask with pipet. Dilute it with 10 ml of distilled water and neutralize the mixture with 1:4 sulfuric acid in the presence of phenolphtalein indicator. Add excess sulfuric acid till the solution become clear and an excess of 0.2 ml of acid. Add 1.5 ml of Fe^{3+} solution and 10 ml of amminium molibdate solution into the flask. Stir the solution with the yellow precipitate and let it settle for ten minutes. Solve the precipitate by the addition of 10 ml of 1:4 sulfuric acid and wait for ten minutes. Add 2 ml of 2 % ascorbic acid to the mixture, make up to the mark with distilled water and swirl. After twenty minutes waiting measure the optical density at 850 nm wavelength. The silica content can be calculated from the calibration curve prepared at the same time.

Calculations

$$SiO_2 \text{ g/l} = \frac{A}{V}$$

where

A : SiO_2 value read from calibration curve (mg)
V : original volume of aluminate liquor sample (ml)

Precision

Variation coefficient is 2.

Time consumption

30 minutes.

15. THERMOGRAVIMETRIC INVESTIGATION OF $Al(OH)_3$

INSTRUMENTATION

The thermogravimetric investigations of alumina hydrate are carried out in MOM type Derivatograph. The instrument is described in chapter 4. of this volume.

AIM OF INVESTIGATION

The investigation is carried out in order to study the thermal decomposition of alumina hydrate during the calcination process. The phase transformation proceeding during calcination is described in volume 2. αAl_2O_3 is formed through different Al_2O_3 modifications from the alumina hydrate as a result of heating.

Transformations of $Al(OH)_3$ connected to H_2O loosing can be followed, and the actual formation temperature of αAl_2O_3 can be obtained by thermogravimetric investigations. Using mineralizers, the forming temperature and the transformation ratio of αAl_2O_3 - an exotherm peak appearing in DTA curve - can be decreased and the physical properties of alumina modified.

INVESTIGATION

In the course of this exercise the sample obtained from the precipitation test (chapter 14.) is to be investigated thermogravimetrically. The investigations are to be carried out without any aid and with 1 wpct $AlCl_3$ mineralizer addition, calculated on Al_2O_3 content of the hydrate.

Weigh 1.000 g alumina hydrate (or a homogenous mixture of alumina hydrate and the mineralizer at investigation with mineralizer), dryed at 110 °C, into the ignition crucible.

Adjust TG sensivity (a practical value is 500 mg) and the heating velocity. Go on with heating to about 1,200 °C as a final temperature.

EVALUATION OF RESULTS

Evaluation is done similary as it is written in chapter 4.

1. Determine the temperatures of different water loosings on the basis of DTA and DTG curve peaks.
2. Determine the weight of lost water at different stages in mgs and convert it into moles.
3. Determine the forming temperature of αAl_2O_3 at ignition in presence of mineralizer on the basis of the appearing exotherm peak in the DTA curve.

16. DETERMINATION OF THE SPECIFIC SURFACE AREA

VOLUMETRIC-DYNAMIC METHOD (PERKIN-ELMER SHELL SORPTOMETER)

In the course of specific surface area determination with the volumetric-dynamic method, a mixture of gases containing an adsorbed and a non-adsorbed gas is passed over the sample. The concentration and related partial pressure of the adsorbed gas in the gas mixture is measured before and after passing over the sample. From this two data the adsorbed gas quantity and the specific surface area are calculated. (Detailed description see in Vol.5.)

The instrument is suitable for determining the specific surface area of bauxites, aluminas and red muds of specific surfaces higher than 0.5 m^2/g.

ANALYSIS PROCEDURE

Sample Preparation

The purpose of sample preparation is to clean the surface of the alumina from pollutants (adhesive water and gases adsorbed on the surface), having disturbing effect on the analysis without changing the structure of the sample.

In the course of preparation of alumina samples the material weighted in the sample tube is placed into a baking oven. It should be dried at a temperature of 110 ± 3 °C for 12 hours and further two hours with flowing helium gas through the sample tube with a flow-rate of 50 ml/min. (Fig.8.28).

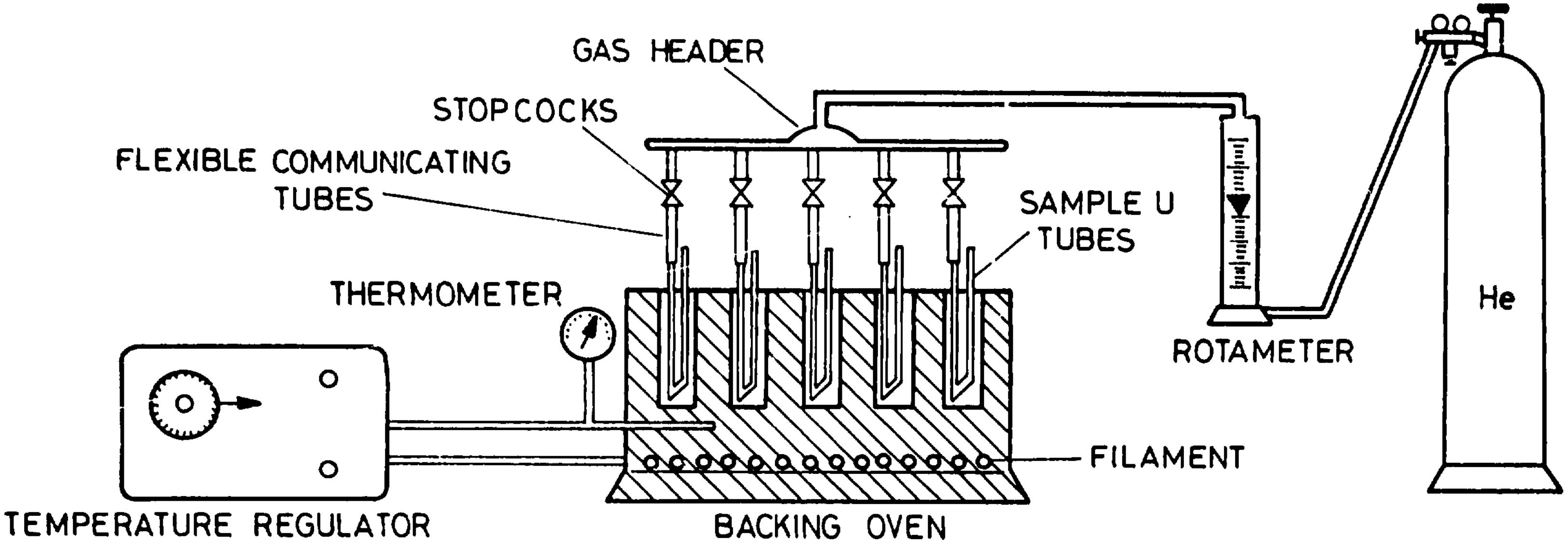


Fig. 8.28

SCHEMATIC DIAGRAM OF THE SAMPLE PREPARATION ARRANGEMENT

Detailed outline of the sample preparation:

1. Clean and dry the sample tube (Fig.8.29)
2. Cap the closing tubes of the suitable numbers to the sample tube, cleaned formerly.
3. Weigh the sample tube.
4. Fill the sample into the tube with a clean, dry funnel.
5. Remove one of the rubber policemen from the tube. Put the rubber policemen into a clean beaker and connect the tube with one end to the overhead manifold of the baking oven.
6. Put the tube into the baking oven.
7. Remove the other rubber policemen too.
8. Turn on the baking oven.
9. Set the temperature regulator switch on 110 °C.
10. When the sample has been baked out (usually 12 hours), open the valve of the helium cylinder.
11. Set the helium pressure to the value of 5 atm, then with the aid of a needle valve set the required flow rate ($\sim$ 50 ml/min).

The sample has to be baked out at least two hours with helium gas flow. Then the preparation procedure has been finished, the sample is ready for analysis.

Description of the Instrument

In the course of the laboratory practice, the specific surface area is determined by Perkin-Elmer-Shell Sorptometer operating on the basis of the volumetric-dynamic principle.

The instrument is suitable for determining the specific surface of 0.5 - 2,000 m^2/g. Nitrogen is used as adsorption, helium as carrier gas. Fig.8.30.

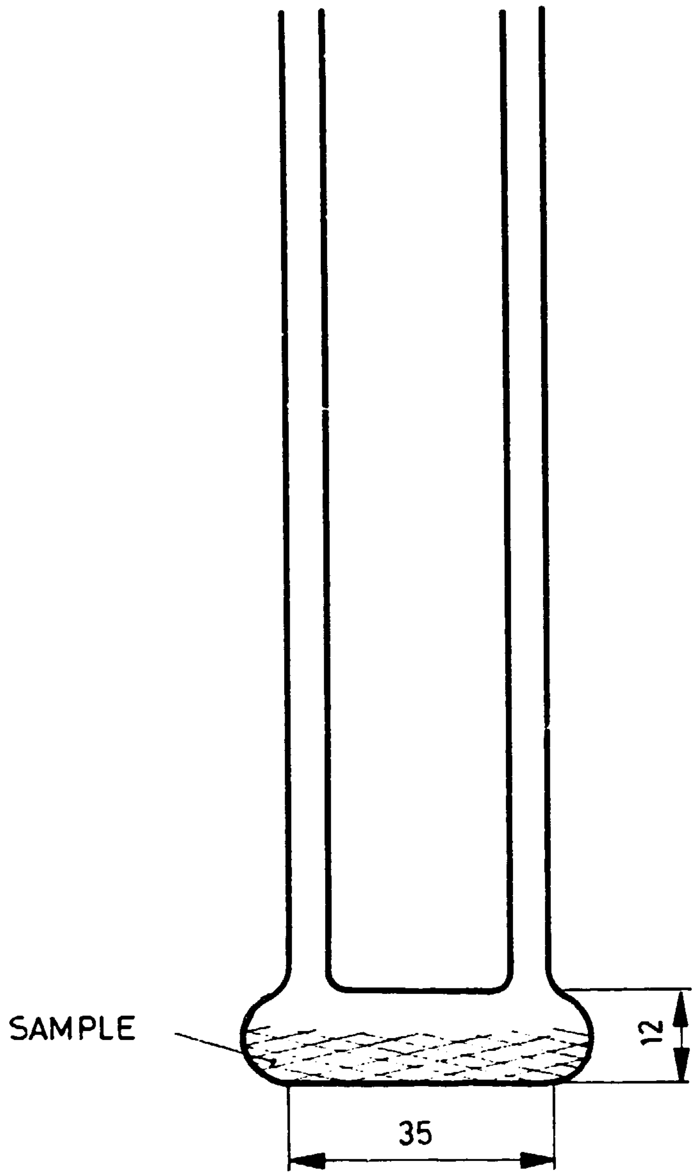
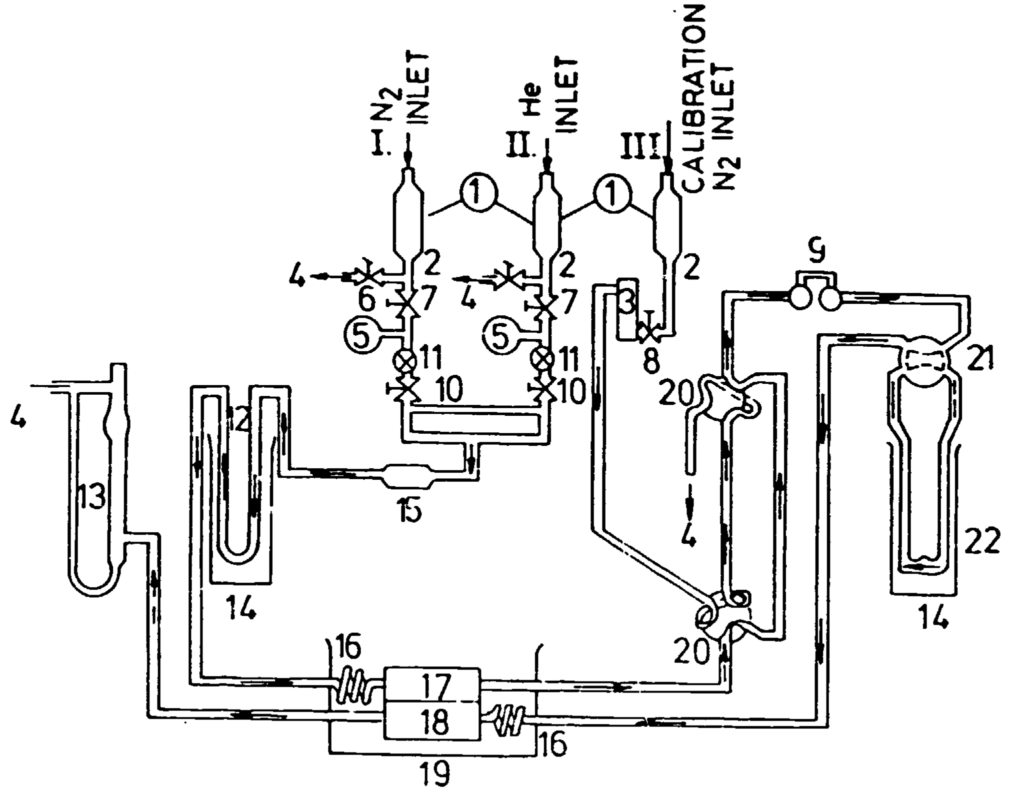


Fig. 8.29

SAMPLE TUBE OF THE PERKIN-ELMER SHELL SORPTOMETER



1. DRYERS
2. FILTERS
3. FLOW METERS
4. VENT
5. PRESSURE GANGES
6. SAFETY VALVES
7. PRESSURE REGULATORS
8. CALIBRATION NEED VALVE
9. MANIFOLD
10. SHUT-OFF VALVES
11. RESTRICTORS
12. COLD TRAP
13. SOAP BUBBLE FLOW METER
14. DEWAR FLASKS
15. MIXING TANK
16. HEAT EXCHANGERS
17. INPUT DETECTOR
18. OUTPUT DETECTOR
19. TANK OF THE TEMPERATURE STABILIZATION BATH
20. CALIBRATION VALVE
21. BY-PASS VALVE
22. SAMPLE TUBE

Fig. 8.30

FLOW DIAGRAM OF THE SORPTOMETER

The instrument consists of a measuring unit, a recorder and a printing integrator. The components of the gas mixture - nitrogen and helium - are introduced into the system through joints and reach the mixing tank through dryer, filter, pressure regulator, pressure gauge and restrictors. The proportion of components and related partial pressures are set on the required value with the aid of pressure regulator valves and pressure gauges. From the mixing tank the gas mixture of given composition passes through a cold trap serving for gas cleaning, the first detector, the sample tube and the second detector after which it reaches the soap bubble flow meter serving for measuring the flow rate, and finally it leaves the system.

In case of steady gas-flow, a gas mixture of the same composition passes through the thermal conductivity detectors mounted before and after the sample, which are in Wheatstone-bridge arrangement. Than the Wheatstone-bridge is balanced, so that the base line on the recorder has zero value. After this the sample tube is immersed into liquid nitrogen. The cooling sample adsorbes nitrogen and the composition of the gas mixture changes indicated by the detector after the sample. The recorder regulated by the Wheatstone-bridge registers a peak which is proportional to the quantity of the adsorbed gas. After reaching adsorption equilibrium the bridge is rebalanced, the recorder reaches again the zero base line. Thereafter the cooling bath is removed and the desorption of the gas is started. The desorption is recorded by the instrument as a peak proportional to the desorbed gas quantity. After the sorption processes, a known amount of the calibration gas is introduced into the gas mixture, by switching on the calibration valve. The balance of the bridge is again broken and a peak proportional to the calibration gas quantity is registered by the recorder. Fig.8.31.

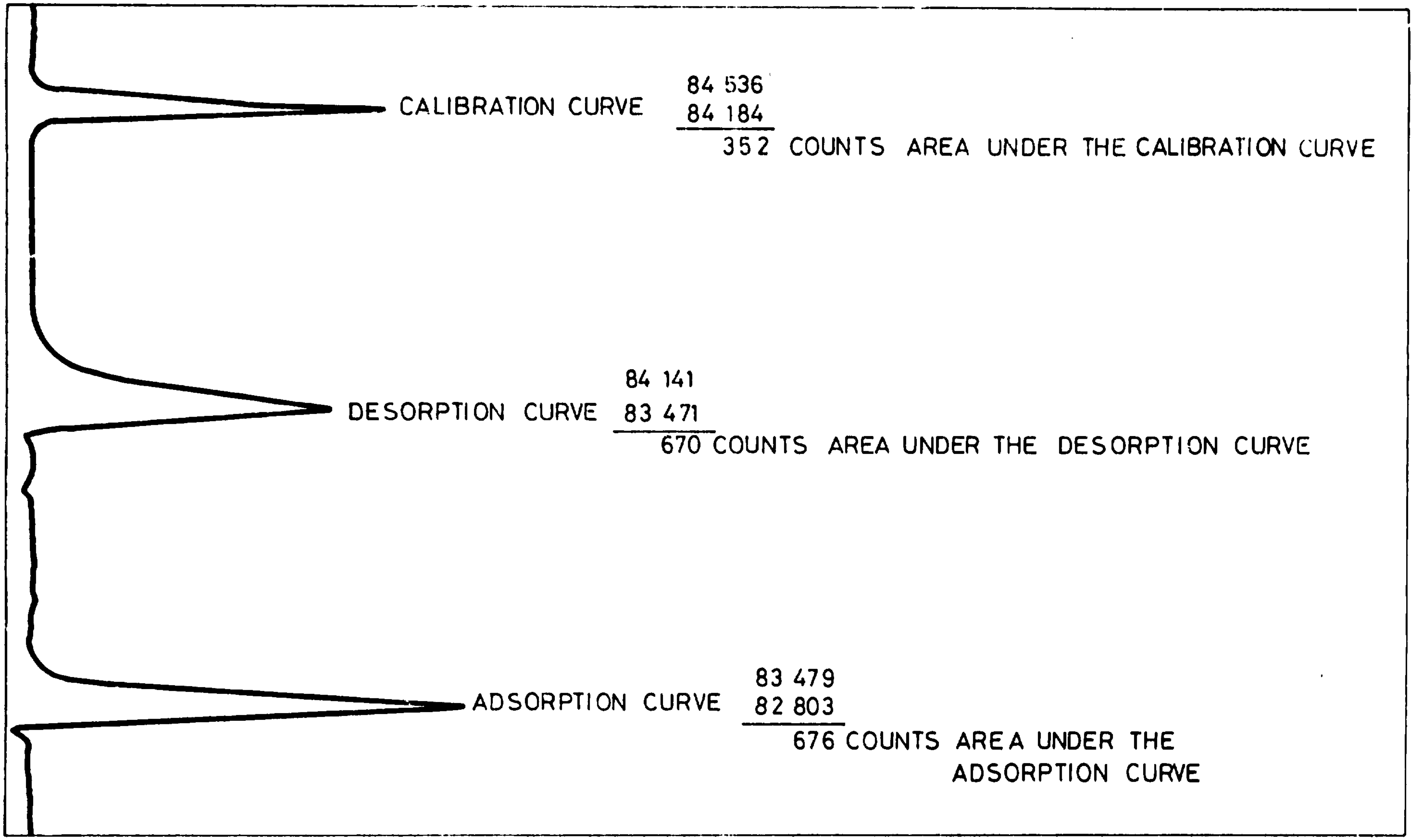


Fig. 8.31

SORPTOGRAM OF THE INSTRUMENT PERKIN-ELMER SHELL

Detailed Description of the Analysis Procedure

1. Connect the soap bubble flow meter to the instrument.
2. Open the valves of the three gas-cylinders connected to the instrument
   a) He carrier gas
   b) N_2 calibration gas
   c) N_2 measuring gas

   Open the needle valves of the three reducers.
3. Fill the three cold traps with liquid nitrogen.
4. Turn on the instrument.
5. Turn the ATTENUATION switch from OFF position (through B) to S position.
6. Turn on the recorder (on the right), (on the left: switch of the paper chart).
7. Turn on the integrator (on the right upper side from OFF to STAND BY position).
8. Set the reductors of the helium and the nitrogen cylinders on the value of 1.4 atm.
9. During this time determine
   a) the room temperature (T_r $^oK = {}^oC + 273$)
   b) the barometer pressure (p_T)
   c) the saturation pressure of the liquid nitrogen (p_o)
10. Shut off the nitrogen stream and adjust the helium stream by setting the GAS MIXTURE 2 pressure regulator with the aid of valves to give a reading of about 22 inches of water on the gauge. Fix the nut bolts.
11. Allow to flow the helium for 10 minutes. During this time control the value of the pressure (1.4 atm.) on the gauges of the three cylinders.
12. Record the flow time of the helium successively three times (22 t_c).
13. Set the nitrogen pressure (GAS MIXTURE 1) on the value corresponding to the first point. It is usually 5 inches of water. Fix the nut bolts.

14. Allow the nitrogen to flow for 10 minutes. During this time control the value of the pressure (1.4 atm.) of the three gas cylinders.
15. Record the flow time of the gas mixture three times (5 t_t).
16. Set the ATTENUATION switch from S to X_1 position. During this time adjust zero value on the recorder with the ZERO switch.
17. Switch on the drive motor of the paper chart of the recorder (on the left side). The recorder draws a horizontal straight line till about three minutes.
18. Turn the main switch of the integrator to MANUAL position.
19. If the pen drawing a horizontal line deviates from zero (in three minutes), reset this value with the zero switch of the Sorptometer.
20. If the Stroboscop is turning, stop it with the ZERO ADJUST switch of the integrator. If this condition remains for three minutes, calibration can be started.
21. Calibration of the instrument
    Open the door of the recorder. Shut off its two switches. Adjust the needle manually from zero to loo value and stop the stroboscop disc with the 100 % ADJUST button. Turn on both switches of the recorder. Shut the door. The needle has to re-set from loo to zero position. If not, repeat the calibration.
22. Switch the valve on the right side of the Sorptometer from SAMPLE to BYPASS position.
23. After connecting the sample tube containing the examined material re-set this switch to SAMPLE position.
24. Wait until zero line is registered by the recorder and the Stroboscop disc is stopped. If it is not so, adjust with zero switch till this condition is realized.
25. Turn the POLARYTY switch of the Sorptometer to the left.
26. Turn on AUTO position the switch of the integrator.

27. After taking care that horizontal zero line is registered by the recorder and the recorder and the Stroboscop disc is not turning, the sample tube is immersed into liquid nitrogen and let in it for cc. 8-10 minutes.
28. When the recorder begins to register a peak, the printing integrator prints a number. For safety's sake push the PRINT button, as it can happen that the automatic number printing fails.
29. After resetting the recorder pen on the zero line /i.e. finishing the peak/ push again the PRINT button, the integrator prints again a number. Write the difference of the two numbers.
30. After passing 8-10 minutes /by the zero line/ take off the liquid nitrogen cooling. Meantime turn the POLARITY switch to the right.
31. Set again the recorder pen on the zero base line so that the Stroboscop disc should not turn. /Adjust with the ZERO switch./
32. Push again the PRINT button. The integrator prints a number.
33. The recorder registers a peak /desorption peak/.
34. After reaching the highest point of the curve, immerse the sample tube into water.
35. After finishing the curve, push again the PRINT button. The integrator prints a number. The difference of the two numbers gives the area under the desorption peak.
36. Take off the water bath from the sample tube.
37. Check the recorder. Does it register zero base line, does the Stroboscop disc stand?
38. Screw home the INJECT switches /1+2/ to the right. Introduce the calibration gas. The recorder of the instrument registers a peak, proportional to the quantity of the calibration gas. The instrument prints a number in the beginning of the peak automatically, in the end push the PRINT button. The difference of the two numbers gives the calibration value. /1+2/
39. Return both checking buttons to CHARGE position.
40. Stop the motor of the paper chart.

41. Turn the integrator main switch from AUTO to MANUAL position. With this the determination of the first point is finished.

Determination of the Second Point

42. Control the quantity of the liquid nitrogen in the two cold traps.
43. Control the 1.4 atm pressure value on the reductors of the three gas cylinders. If it is not so, adjust it.
44. Control that the helium pressure is on 22. If it is not so, adjust it.
45. Set the nitrogen pressure to the second value. In our practice it is 8 inches of water.
46. Wait for 10 minutes meanwhile controlling the 1.4 atm pressure value on the three reductors.
47. Record the flow-time successively three times /8_{t_t}/.
48. Turn on the paper chart of the recorder according to point 17.
49. Turn the POLARITY switch of the Sorptometer to the left.
50. Turn the MAIN switch of the integrator from MANUAL to AUTO position.
51. After this repeat from the 27th point.

The determination of the third point is carried out simultaneously. In this case the nitrogen pressure has to be set to 10 inches of water.

After finishing the analysis, the order of switching-off is the following:

1. Turn the integrator main switch to OFF position.
2. Turn both switches of the recoder to OFF position.
3. Turn off the ATTENUATION switch of the Sorptometer.
4. Disconnect the instrument.
5. Close the reductors of the three gas cylinders.
6. Close the connecting pipes of the three gas cylinders.

7. Empty the liquid nitrogen from all cold traps.
8. Release the gas flow meter, flush the glass tube.

CALCULATION OF THE SPECIFIC SURFACE AREA

The determination of the specific surface area is based on the areas under the peaks: the proportions of the areas under the sorption and calibration peaks equal those of the quantities of the sorption and calibration gases. The surface area is calculated by the aid of the desorption peak. The volume of the calibration valve is known, so from the proportion of the peak areas the quantity of the desorbed gas /V_{des}/ can be calculated by the simple equation:

$$V_{des} = \frac{A_{des}}{A_{cal}} \cdot V_{cal} \qquad /1/$$

where: A_{des} = area under the desorption peak

V_{des} = desorption volume

A_{cal} = area under the calibration peak

V_{cal} = volume of the calibration gas in ml

$V_{cal\ 1}$ = 0.2504 ml

$V_{cal\ 2}$ = 0.2276 ml

$V_{cal\ 1+2}$ = 0.4868 ml

The correction factor recalculating the calibration gas volume for normal conditions:

$$f = \frac{P_T \cdot 273.16}{760 \cdot T_R} = 0.3595 \frac{P_T}{T_R}$$

where: P_T = atmospheric pressure in Hgmm

T_R = room temperature in ^{O}K

The desorbed normal gas quantity:

$$V_{des} = \frac{A_{des}}{A_{cal}} \cdot 0.3595 \frac{P_T}{T_R} V_{cal} \qquad /2/$$

Putting this value into the BET equation /see Vol. 11./ the value of V_m is obtained:

$$V_m = \frac{A_{des}}{A_{cal}} \cdot \frac{P_T}{T_R} \cdot V_{cal} \cdot 0.3595 \, /1 - \frac{p}{p_o} / \, /1 + \frac{\frac{p_o}{p} - 1}{240} / \qquad /3/$$

where: $p = \frac{F_a}{F_t} \cdot p_T$

p = partial pressure of the nitrogen in the gas mixture

F_t = flow rate of the gas mixture in ml/min

$$F_t = \frac{60}{t_t} \cdot V_{meter}$$

V_{meter} = volume in the soap bubble flow meter between the two calibration marks

$$V_{meter} = 20.09 \text{ ml}$$

t_t = soap film transit time for the gas mixture /sec/

F_a = flow rate of the adsorbed nitrogen gas (ml/min)

$F_a = F_t - F_c$

F_c - flow rate of the helium (ml/min)

$F_c = \frac{60}{t_c} \cdot V_{meter}$

t_c - soap film transit time for helium (sec)

After determining the V_m value, the specific surface area can be calculated from the 4th equation:

$$S = \frac{V_m \cdot 4.3529}{W} \qquad /4/$$

where: W = sample weight in g

From the specific surface values obtained from the three measuring points, the mean error of the middle value is given by the following relationship:

$$h = 100 \cdot \sqrt{\frac{\sum_{i=1}^{n} /\bar{S}_m - S_{mi}/^2}{n/n-1/}} \quad \bar{S}_m \qquad /\%/ \qquad /5/$$

where: $\bar{S}_m$ = average of the measured values

S_{mi} = result of the individual determinations

n = number of the determination

In the practice the evaluation of the results is performed with the aid of a program, made for the pocket calculator Texas Typ. Sr-52.

The instructions for use of the program is the following:

1. Read side A of the magnetic card containing the constants of the calculation. Put the card (Program No. 1.) into the hole on the right side of the calculator and read if with pressing the following keys:
   CLR - 2nd - Read
2. Run the constants giving program with pressing the key 'A'.
3. Read the sides 'A' and 'B' of the calculating card:
   side 'A': CLR - 2nd - Read
   side 'B': 2nd - Read
4. After pressing the key 'A' the order of the results is the following:
   value p_o - RUN - value p_T - RUN - value T_R - RUN -
   - value W - RUN
5. After pressing the key 'B' give the results obtained for the individual points in the following order:
   value t_t - RUN - value t_c - RUN - 1, 2, 3 /calibration volume used/ - RUN - A_{des} - RUN - A_{cal} - RUN
   The calculated surface value on the display can be seen.
6. The surface values of the other points are obtained with the respective data, as in point 5.
7. The calculation of the average and the error is performed with pressing the key 'E'.
   'E' - S_{cal} - RUN - h_{cal}

17. DETERMINATION OF PHYSICAL PROPERTIES OF ALUMINA

DETERMINATION OF ALUMINA PHASE COMPOSITION BY CRYSTALOPTICAL METHOD

PRINCIPLE OF DETERMINATION

The phase transformations of alumina hydrate during calcination are followed by increase in the refraction rate. A method developed for α Al_2O_3 content determination is based on this phenomena which can be easily carried out and fairly well reproduced.

That simple method is very useful when there is not an up to date X-ray diffractometer - adequate to the modern alumina analyser requirements and expensive - available.

The essence of the method is that when a crystal of unknown refraction rate is immersed into a liquid of known refraction rate, a relief, the so called Becke line appears and it moves towards the material of higher refraction rate when raising the eye-piece. The refraction rate of α Al_2O_3 is between 1.752 and 1.768. The most suitable liquid for immersion is methylene-iodide (n = 1.74), not only because of its appropriate refraction rate but of its relative stability. (Its refraction rate does not change during rest.) Phases of higher refraction rate than 1.74 are called α alumina. The other phases are summarised under the name γ alumina.

The relief of α Al_2O_3 is definitely positive, immersed in a liquid of 1.74 refraction rate (raising the eye-piece, the Becke line is moving inwards the grain) and it has a light blue color.

Transiant Al_2O_3 phases of lower refraction rates have a negative relief and their color is yellow-brownish.

It is to be noted that the materials of higher refraction rate than 1.74 can be only presumably called α Al_2O_3 because only the α Al_2O_3-rich fraction of the sample is determined by this method.

So the statistical distribution of different alumina phases is determined by counting alumina particles of different crystal-optical properties.

EQUIPMENT AND ACCESSORIES

a) A transmission microscope with all accessories
b) A suitable counting equipment
c) Methylene-iodide, refraction rate = 1.740 (Must be freshly distilled and faint colored)
d) Objective cover sheets made of glass.

DETERMINATION OF THE PHASE COMPOSITION OF AN ALUMINA SAMPLE

a) Sampling and averaging. Diminish the sample to 0.3 g by quartering.
b) Preparation of the sample for microscoping. Sweep a little amount of alumina on the objective sheet using a small brush, cover it with the cover sheet and drop a little methylene-iodide to the side of the sample. Moving the sheets, help the grains distribute equally and immerse into the liquid.
c) Investigation with microscope. Fix the prepared sample under the objective lens and analyse at 300/600x magnifying. Use a cross line eye-piece for counting the particles of different phases.
d) Determination of α Al_2O_3 percentage. Grains of higher refraction rate than 1.740 show a light blue color through microscope, and the Becke line located at the edge of the grain moves towards the middle of the grain

when raising the eye-piece. (Fraction I.)
Grains of smaller refraction rate are yellow and the Becke line moves inversely repeating the operation written above (Fraction II.). Separate the two phases on the basis of the operation written above.
Determine the number of grains of fractions I. and II. by counting the spots, taking only those grains into account which are on the cross line.

PRESENTATION OF RESULTS

A valvular equipment is used for counting. The distribution of phase fractions can be concluded only after counting 1,000 points at least. If fraction I. is point A
fraction II. is point B
and their sum is point C, the percentage of α alumina is calculated as follows:

$$X_1 = \frac{A \cdot 100}{C} \%$$

Since all of the grains which were not classified as α, are classified γ, the percentage of γ alumina is:

$$X_2 = (100 - X_1), \quad \%$$

If a more accurate analysis is needed, the ratio of I. and II. fraction inside a grain must be determined also because the grains are also heterogenous very frequently. Depending on the phase ratio inside the grain, the valvular must be stroken by the following:

These properties are dependant on the grade of calcination as far as the better calcined alumina, and the alumina calcined with mineralizer aids are more fragile and break into smaller grains of irregular surface in the kiln and even more during pneumatic transportation.

The angle of repose of different aluminas differs from 30° to 60° (Vol.5. p.5-98.) dependant on properties described above.

PRINCIPLES

Rough alumina of air dry condition is let to flow through a funnel of definite size from a given height without being shaken to a definite horizontal sheet and the foot angle of the formed cone will be determined.

EQUIPMENT

The equipment shown in Fig. 8.32 consists of the following parts:

FUNNEL, made of stainless stell, equipped with a metal sieve, which is fixed by screwing together the two parts of the funnel. The outer shell of the lower part of the funnel is screw-threaded and it is driven into its holder. Minimal inside diameter of the funnel is 6 mms.

BASE-SHEET, made of stainless steel or other non oxidizing metal possibly marble, minimal size 200 x 270 mms, surface is polished, can be fixed horizontally without being shaken, and it is marked by two mm scaled lines intersecting each other under the origo of the funnel. A pin is formed in that point to set the height. The base-sheet is fixed to 3 screws which serve the horizontal adjusting of the sheet.

FUNNEL-HOLDER, made of stainless steel, it is fixed to the base-sheet so that the immaginar shaft of the funnel intersects the base-sheet rectangular at the origo pin.

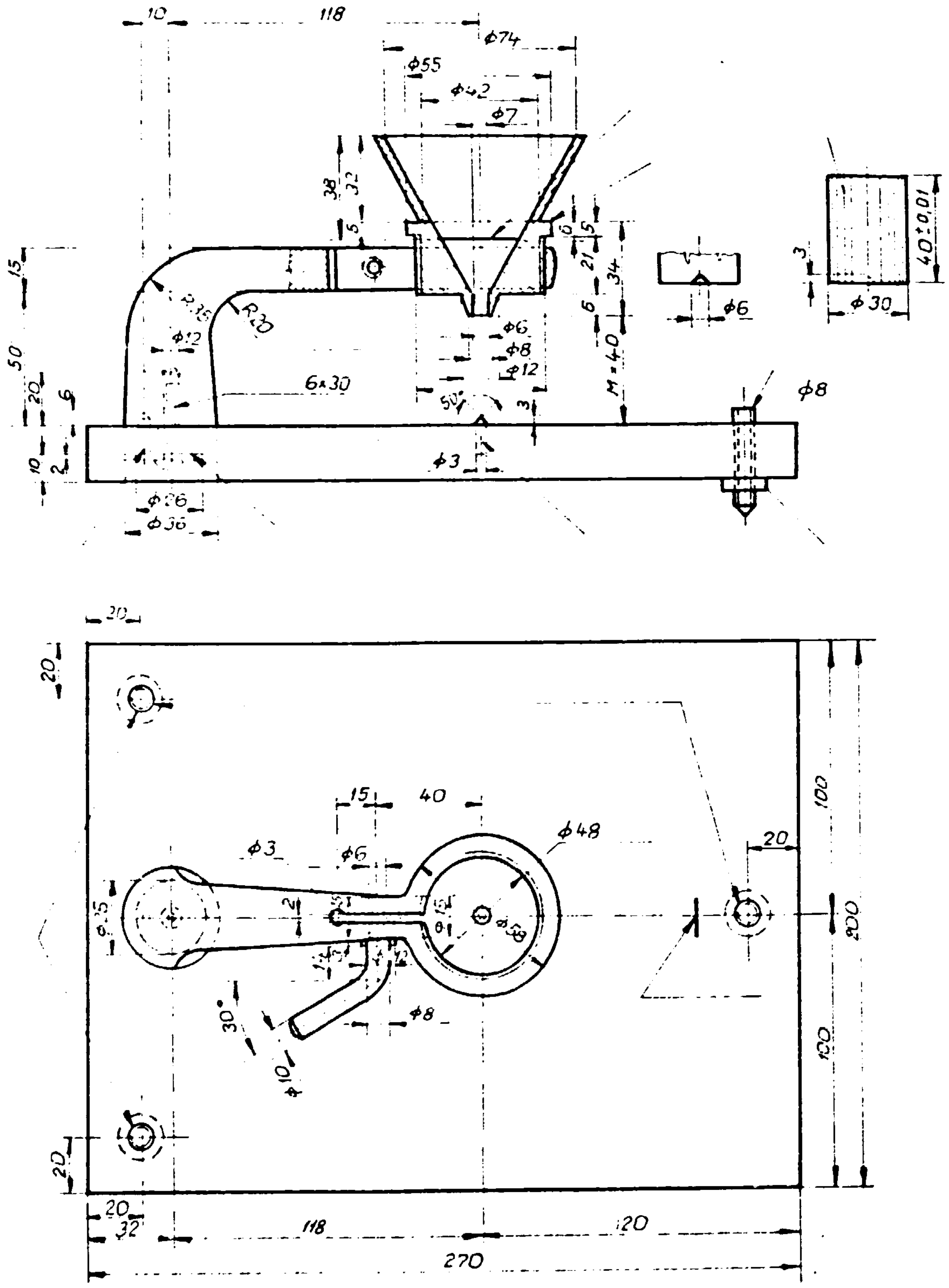


Fig. 8.32

EQUIPMENT FOR DETERMINING THE ANGLE OF REPOSE

EXPLANATION TO Fig. 8.32

Equipment for determination of angle of repose alumina

1. screw-threaded
2. empty metal sieve, hole diameter: 1 mm
3. made of bronze or brass
4. height adjusting cylinder
5. adjusting screw
6. screw-threaded nut
7. concealed into lead
8. metal washer
9. screw
10. fixing screw
11. central notch concealed into lead
12. location of adjusting screws
13. screw-thread
14. shaft of watergauge

Part in the aggregate		Strokes on valvular	
Frac I.	Frac II.	Frac. I.	Frac. II.
4/4	-	4	-
3/4	1/4	3	1
1/2	1/2	2	2
1/4	3/4	1	3
-	4/4	-	4

In this case 4,000 strokes present 1,000 grains.

ANGLE OF REPOSE DETERMINATION

INTRODUCTION

The physical properties, like αAl_2O_3 content, apparent density, specific surface area, angle of repose, benzene number, density, which serve as grade numbers of alumina, show only tendencies of coherences. The properties can be classified into two groups. Properties connected to crystalline structure belong into the first one. So the density is increasing and the specific surface area is decreasing by the increase of αAl_2O_3 content but the benzene number, angle of repose and apparent density do not show any coherence to the αAl_2O_3 content - especially not when it is between 75 and 90 pct.

Properties connected to the size, shape and surface of the grains are classified into the other group. Alumina of fine grains (floury alumina) is adhesive, the angle of repose, the benzene number and the apparent density of it is higher than those of coarser (sandy) alumina.

Height adjusting cylinder, a 400 mm high cylinder, made of stainless stell, base and top polished, has a notch in the base fitting the origo pin.

DETERMINATION

Adjust the base line horizontal with the adjusting screw, check it with a gauge. Fit the height adjusting cylinder to the origo pin of the base-sheet and screw the funnel into the holder as far as the funnel hits the height adjusting cylinder. After this remove the cylinder and put it aside.

Pour the air-dry, raw alumina sample of room temperature into the middle of the funnel from about 40 mms height, taking care of not shaking the equipment.

The alumina flow is to be between 20 and 60 gs per minute. If the alumina flow gets jammed at the sieve, help with a small brush without shaking the equipment.

Finish the alumina-inflow when the top of the alumina cone reaches the funnel. So a frustum cone will be formed which has a 6 mms diameter upper sheet.

Mark the foot of the alumina cone round (with a pencil), read the length of the 4 diameters of the cone.

COMPUTATION OF RESULTS

Angle of repose in degrees (R) is calculated in the following way:

$$R = \text{arc tg} \frac{2H}{D - d}$$

where H height of alumina cone, namely the distance between base sheet and outfall stub of the funnel (mm)

D arithmetical mean of the 4 diameters (mm)

d inside diameter of the outfall stub of the funnel (mm)

Note

In case of a unit prepared on the basis of the given dimensions, a simplified formula is obtained, as follows:

$$R = \text{arc tg } \frac{80}{D - 6}$$

TEST TOLERANCE

The difference between the arithmetical mean of 3 tests and the unique tests must be less than $\pm 1.5^{\circ}$.

DETERMINATION OF APPARENT DENSITY

PRINCIPLES

Air-dry, raw alumina is let to fall into a cylinder of known volume standing on a horizontal base and not shaking. The mass of alumina and water of known volume will be balanced and the ratio of the two masses will give the apparent density.

EQUIPMENT

FEEDING FUNNEL, made of glass, or plastic or polished, stainless steel; its parameters are:

inside diameter	10 mm
cone angle	60 °
stem length	8 mm
stem inside diameter	6 mm

OFF HOLDER VESSEL, made of glass or plastic or polished, stainless stell, is a plain cylinder of 200 ccm volume, height-diameter ratio is about 6 to 1.

DRIVING SHELL, made of glass, or transparent synthetic material, inside surface smooth, both ends of the cylinder are open, height 10 cm.

ADJUSTABLE HOLDER RING,mounted to a scaffold for fixing the feeding funnel to an appropiate position.

DETERMINATION

Determination of the volume (water value) of the off holder vessel. Weight the mass of the empty vessel with 0.05 g accuracy, put on flat base, pour distilled water of room temperature to the brim. The difference of the two values is the water value which is considered to be the volume of the cylinder.

Note: density of water is not taken into consideration because it does not change the results inside the accuracy range of the determination.

Determination of the mass of known volume alumina. Determination is carried out with a dry, shaking-fix cylinder standing on a plane base, at room temperature and air-dry, raw alumina of room temperature is used to it.

Put the off holder vessel on a shaking-fix plane, horizontal base, mount the feeding funnel with the adjustable holder ring to the fix standing scaffold so that the stem stub of the funnel should be have the same shaft of the off holder cylinder and the distance between the edge of the cylinder and the outfalling stub of the funnel should be 10.0 cm. Place the driving shell on the edge of the cylinder (in/outside diameters are the same) so that it is close to the outfalling stub of the funnel but do not touch it. Let the airdry, raw alumina sample flow into the middle of the funnel from 4 cm height above the funnel, with a constant flow taking care of not to shake it meanwhile. The alumina flow is to be 20-60 gs per minute.

Note: if the alumina flow got jammed in the funnel stem stub it through with a piece of wire, taking care of not to shake it.

Stop feeding alumina when the cone formed by falling alumina rises above the edge of the cylinder. Remove the alumina excess above the cylinder volume so that lift the funnel with the adjustable holder ring and pull the driving shell lightly, pass the hold-off cylinder without moving it.

Clean the cylinder outside and weight its mass with 0.05 g accuracy.

COMPUTATION OF RESULTS

The apparent density (L) is determined by the following formule as a ratio of the mass of alumina and the mass of water of the same volumes.

$$L = \frac{G_A}{G_W} \text{ , } g/cm^3$$

where G_A alumina mass of given volume (g)
G_W water mass of given volume (g)

TOLERANCE

The admissible maximum difference between parallelly made determinations is 1 relative pct.

18. DETERMINATION OF GRAIN SIZE DISTRIBUTION OF $Al(OH)_3$

INTRODUCTION

There are two ways to determine the grain size distribution of powderlike materials, the direct and the indirect method. In the present exercise we will determine the grain size distribution of an alumina hydrate sample washed and dried for the purpose of determination with air-jet sieve serie - direct method - and turbidity measurement with photoextinction sedimentometer - indirect method.

GRAIN SIZE DISTRIBUTION DETERMINATION WITH AIR-JET SIEVE SERIE

The operation principle of an Alpine made air-jet sieve shown in Fig.8.33 is the following: the dry sample is placed on the sieve and the grains smaller than the sieve opening are transported by and air-jet to the collector. The air-jet blows the sample from under the sieve through a rotating slot, of sieve opening radius length. The fine grains pass through the sieve opening downwards and can be collected on a filter below the sieve (see Vol.5. Chapter 5.)

Sieving is carried out by the so called negative order on the sieve serie. It means that 50 gl of the sample is placed on the finest sieve and after air-jet sieving the residual material will be weighed. After that the sieve will be changed for the finest but one, and the operation will be repeated with the weighed residual sample. Only one sieve plate can be used for one air-jet sieving. By weighing the residual material on certain sieves, the points of the sieve residue curve can be gained directly.
Plot the distribution and the frequency curves of grain size on the basis of the analysis.

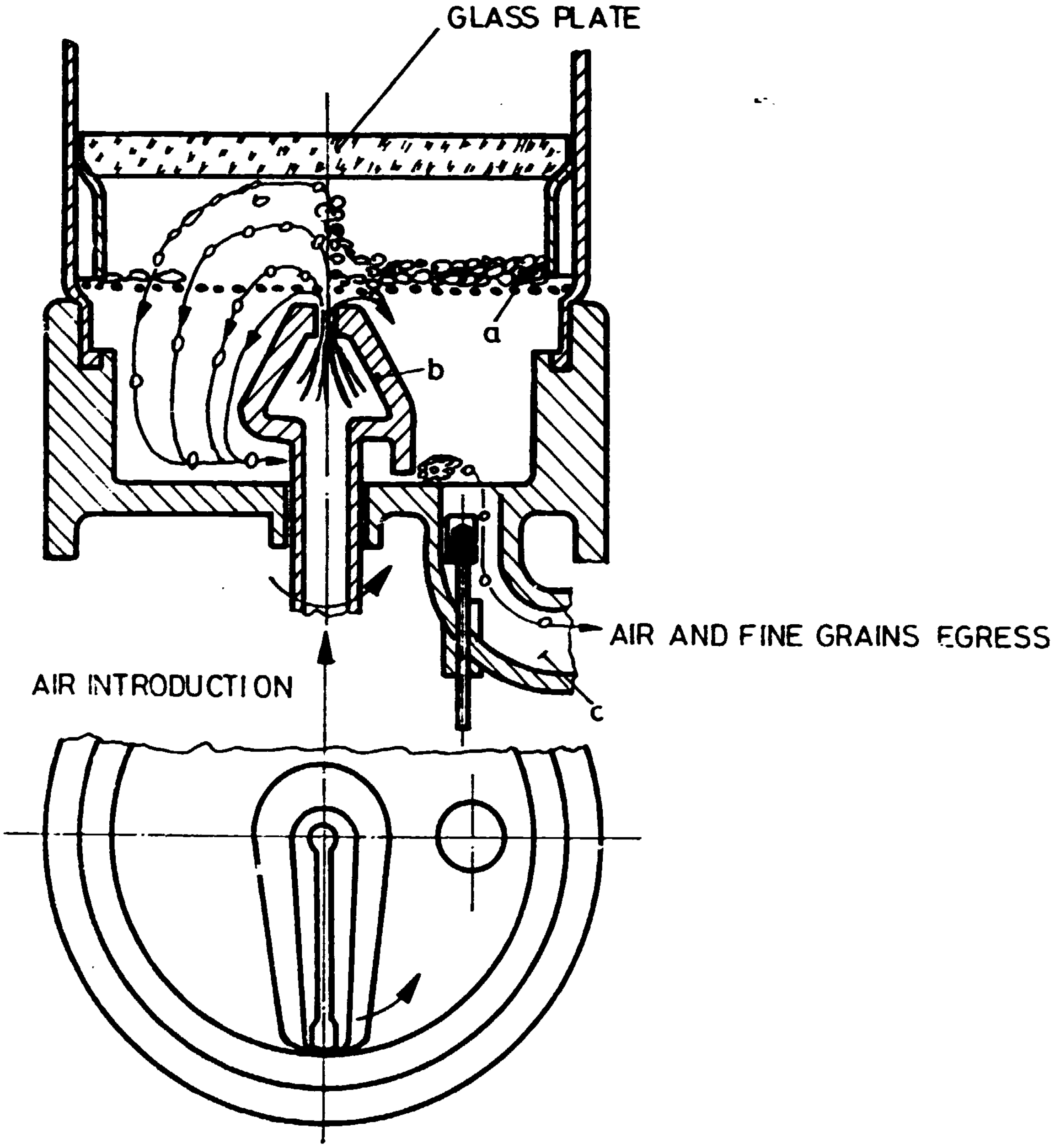


Fig.8.33

OPERATION PRINCIPLE OF AN ALPINE AIR-JET SIEVE

$Al(OH)_3$ GRAIN SIZE DISTRIBUTION DETERMINATION BY PHOTOEXTINCTION SEDIMENTOMETER

Determine the grain size distribution of the $Al(OH)_3$ sample used for the previous test by a photoextinction Sedimentometer type EEL. Look up the determination principles in Vol.5. the operation and the important parameters of the instrument EEL are described in the brochure enclosed to the instrument.

Carry out the determination in the following way:

- Clean the sedimentation cells thoroughly and perfectly, dry them, wipe the outer surface of the shorter side till it becomes bright, taking care of not to touch these sides any more.
- Pour suspension liquid (30 vpct glycerine distilled water solution) up to desired height (h = 4.0 cm).
- Place the cells to the cell holders of the sedimentometer. Put the reference cell to the holder No.1 and keep it there to the end of the measuring.
- Let the instrument switched in for half an hour before you start measuring, in order to eliminate disturbing effects.
- Adjust the torsion fibre regulator, having the plugs removed from the front of the galvanometer, so that the hair-line is to be at the infinite (∞) sign of the logarithmic scale (the scale below is linear).
- Read the extinction at given times. The reading times of extinction values are given in Table 18.1 showing the settling times of grains of 110, 90, 70, 56, 44, 36, 28, 22, 18, 14, 11, 9, 7, 5.6, 4.4, 3.2, 2.8, 2.2 diameter in function of the temperature of the suspension liquid.

- Calculate the extinction differences $E_{ti}-E_{ti-1}$ from the extinction values at given times $(E_{ti}-E_o)$. It will belong to the mean of the grain fraction settled out at that interval (d_{mi}).
- The average grain size (d_{mi}) of the fraction is the aritmethical mean of the under and upper limit of the grain size fraction i.
- Read the extinction coefficient (K_m) belonging to d_{mi} from Table 8.10 of the instrument brochure.
- Calculate the weight rates of the size fractions by the following formule:

$$g_i = \frac{d_{mi}\ (E_{ti} - E_{ti-1})}{K_{mi}}$$

The physical meaning of g_i is the elementary surface of fraction i.

- Calculate the weight percents of fractions as follows

$$w_i = \frac{g_i}{\sum g_i}$$

Table 8.10

SETTLING TIME TABLE OF ALUMINA HYDRATE IN 30 WPCT GLYCERINE-DISTILLED WATER SOLUTION FROM h = 4.0 cm

	Temperature °C							
d_s', /um	20	21	22	23	24	25	26	27
110	9"	9"	9"	8"	8"	8"	8"	8"
90	14"	14"	13"	13"	13"	12"	12"	12"
70	24"	23"	22"	21"	21"	20"	20"	19"
56	36"	35"	34"	33"	32"	31"	30"	30"
44	59"	57"	55"	54"	52"	51"	49"	48"
36	1'28"	1'25"	1'23"	1'20"	1'18"	1'16"	1'14"	1'12"
28	2'25"	2'21"	2'16"	2'12"	2'09"	2'05"	2'02"	1'59"
22	3'59"	3'51"	3'44"	3'38"	3'31"	3'26"	3'21"	3'15"
18	5'53"	5'42"	5'31"	5'22"	5'12"	5'04"	4'57"	4'48"
14	9'42"	9'24"	9'05"	8'50"	8'34"	8'21"	8'09"	7'55"
11	15'41"	15'12"	14'47"	14'17"	13'53"	13'30"	13'12"	12'48"
9	24'	23'	22'	21'	21'	20'	20'	19'
7	39'	38'	37'	36'	35'	34'	33'	32'
5.6	61'	59'	57'	55'	54'	52'	51'	49'
4.4	98'	95'	92'	90'	87'	84'	82'	80'
3.2	146'	142'	137'	133'	129'	126'	123'	119'
2.8	241'	234'	226'	219'	213'	207'	203'	197'
2.2	392'	380'	368'	357'	347'	338'	329'	320'

For the sake of sparing time do not determine the size distribution below 7 /um.

Calculation is programmed on a table calculator. After feeding in the extinction values, it prints the size distribution and frequency wpct-s. Using these data plot the grain size distribution and frequency curves of the alumina hydrate sample. Compare with curves obtained from air-jet sieve investigations.

For an example data of an alumina sample grain size distribution determination by sedimentation in distilled water is given in Table 8.11.

After finishing the tests let us get acquainted with an up to date size distribution analyser, a new Fritsch product, Analysette - 20 Sedimentograph. Measuring principles are similar to these for the EEL photosedimentometer, but it is much more quick and has a fully automatized evaluation system.

Table 8.11

DATA OF ALUMINA GRAIN SIZE DISTRIBUTION IN DISTILLED WATER

d_{si}	t	$E_{t,i}-E_c$	$E_{t,i}-E_{t,i-i}$	d_{mi}	K_{mi}	g_i	w_i
2	97'	1					
			1.0	3.5	2.8	1.28	0.08
5	15'35"	2					
			0.5	7.5	2.1	1.78	0.11
10	3'53"	2.5					
			0.5	15	1.9	3.94	0.26
20	58"	3					
			31	25	1.6	484.37	32.16
30	26"	34					
			36	37.5	1.33	1015.02	67.39
45	12"	70					
						1506.39	100.00

19. CHEMICAL ANALYSIS OF ALUMINA

DETERMINATION OF THE TRACE ELEMENTS OF ALUMINA

Determination of SiO_2, Fe_2O_3, V_2O_5 and RiO_2 content of alumina by emission spectrographic method.

PRINCIPLES

The emission spectrographic quantitative analysis is based on the relation between the power of the emitted radiation of a properly selected wavelength and the quantity of the corresponding element in the sample. This relation is quite complicated and depends among others, on the excitation mode and temperature as well as the size, form and material of electrodes.

In the case of emission spectrographic determination of the trace elements of alumina, an air-dry alumina sample is mixed with graphite powder and excited in a cup-formed graphite anode with a dc. are using a specially formed graphite rod as counter electrode. The radiated light is recorded on a photographic plate and the intensities of reference and analyte line pairs are measured with a densitometer after development of the plate. The concentration of the element to be determined can be evaluated from the intensity ratio of analyte/reference line pair vs. concentration curve.

PROCEDURE

By the knowledge of the construction and operation of the Zeiss Q-24 quartz spectrograph, load the plate holder with special plate in complete darkness. Return the holder to the spectrograph and set it at the uppermost position.

It is assumed that the instrument has already been focused, adjusted and is ready to use.

Prepare the sample by mixing it with graphite powder in 1.2 fraction in a corundum mortar. Fill up the hole of the drilled graphite cup like anode (hole size 4 x 3 mm) with this mixture and place it on a sample stand. Take the next sample and prepare it similarly. Place a prepared graphite anode in the arc stand, and a drilled pin like (size 3 x 12 mm) graphite rod as counter electrode too. Adjust the position of the arc stand, so that the distance be 2 mm between the two electrodes and to take the light spot to the slit of the spectrograph. Place the safety slide to the right position. Strike the dc. arc setting the current intesnity to 6 A, open the slit of the spectrograph and take an exposure. Now lower the plate to the next position and repeat the procedure with the sample.

Take the plateholder to the darkroom, bathe the plate 4-8 min in the developer depending on the quality of the plate, then rinse it in water and place it in the fixer for another 15 min. Dry the plate at room temperature.

Measure the blackening of the analyte/reference line pairs with Zeiss microdensitometer according to the user manual.

The selected line pairs can be seen hereunder:

Element	line pairs	concentration range
Si	Si 2516.1/ Al 2669.3	0.005 - 0.1
	2881.6/ Al 3064.3	0.003 - 0.1
Fe	Fe 2598.4/ Al 2669.2	0.005 - 0.1
	2755.7/ Al 3064.3	0.005 - 0.1
V	V 3184.0/ Al 3064.3	0.001 - 0.5
Ti	Ti 3349.0/ Al 3064.3	0.001 - 0.1

CALCULATIONS

The concentration of element to be determined can be read on the calibration curve prepared with accurately analysed standard samples. The blackenings of the analyte/reference line pairs are plotted against the log concentration of the element.

PRECISION

Variation coefficient is about 5-10.

TIME CONSUMPTION

The consumed time depends on the number of samples.

DETERMINATION OF TOTAL SODIUM CONTENT OF ALUMINA BY FLAME SPECTROPHOTOMETRIC METHOD

PRINCIPLE

An air-dry alumina sample is fused with H_3BO_3 flux at 900 ^{o}C in a platinum crucible and the mixture is extracted with diluted hydrochloric acid. The sodium content of this solution is measured by flame photometric method.

PROCEDURE

Weigh 0.5 g of an air-dry alumina sample and mix it with 1.5 g boric acid in a platinum crucible. Heat the mixture at 900 °C for twenty minutes. Let the crucible cool and wash the content to a 250 ml beaker with hot distilled water. Add 25 ml of 1F hydrochloric acid and boil the mixture till the fused material is dispersed. After cooling transfer the mixture to a 100 ml volumetric flask and fill up to the mark. Let the mixture to settle, fill up to the mark and pipet from the clear solution to a 25 ml beaker. Measure the sodium content of this solution. Adjust the SP 1900 AAS instrument properly according to the procedure included in the flame photometric determination of sodium content of red mud using the same standard solution. Use a previously prepared boric acid solution as blank.

CALCULATION

Use a Texas SR 52 pocket calculator to evaluate the sodium content of alumina samples. The program card enclosed contains the data of standard calibration curve and basic equations are needed. Feed the weigh, moisture and intensity data of the alumina sample using the required data file keys and read the sodium content in percent units.

PRECISION

Variation coefficient is about 5.

TIME CONSUMPTION

4 hours/12 sample.

APPLICATION OF THE LECO CS-46 INSTRUMENT FOR THE DETERMINATION OF C AND S CONTENT OF ALUMINA

PRINCIPLE

The LECO CS-46 system is suitable for the determination of carbon content 0.0001 to 5.0 % and sulfur content 0.0001 to 0.4 %. The system consist of three parts, the Electronic Balance EB-25, the Induction Furnace and the Determinator.

A closed loop flow system filled with pure (99.95) oxygen is utilized to burn the sample in the Induction Furnace. Approximately 97 % of the carbon is oxidized to CO_2 and about 3 % burns to CO (except on low carbon samples where very little CO is formed). The sulfur oxidized to SO_2. The gases resulting from combustion are circulated around the loop at high pumping rate and the concentration becomes homogeneous very rapidly. The carbon dioxide (CO_2 Low Range, CO_2 High Range) carbon monoxide and sulfur dioxide contents are measured by IR adsorption. All three gases are detected separately in the same chamber.

The solid state detectors are energy detectors. Filters are used to pass the appropriate IR wavelengths to each detector. In the absence of CO, CO_2 and SO_2 the energy received by each detector is maximum. During combustion the IR absorption of CO, CO_2 and SO_2 gases in the chamber cause a loss of energy; therefore a loss in signal results which is proportional to the concentration of each gas.

PROCEDURE

Sample preparation. Alumina sample dried at 300 °C 2 hours is used for the analysis.

The CS-46 instument is completely automatic, but there is also a possibility to work with manual mode.

1. Push the "Power" switch to the up position 8 hours before beginning the work.
2. Check the temperature of the thermostate, it must be 47-50 °C.
3. Push the "Power" switch of the Electronic Balance (20 minutes before).
4. Open the oxygen the pressure it must be 30 PSI.
5. Push the switch GAS.
6. Push the switch PUMP (loop pressure 4-5.2 PSI).
7. Push the switch "AUTO MODE".
8. Depress and hold the FLUSH switch until the carbon DVM is nearly stable. Release the "FLUSH" switch before proceeding,
9. The Carbon DVM must be indicate between +0.2995 - +3.005. If it is does not, adjust CO_2 Low Gain.
10. The Sulfur DVM must indicate between +0.0002 - -0.0002. If it does not, adjust CO_2 LOW ZERO.
11. Induction Furnace, Filament Voltage on, High voltage on.
12. Place the crucible on the EB-25 Balance poin.
13. Depress the TARE switch on the AWC control box.
14. Add about 0.5-0.7 g alumina sample to the crucible.
15. Depress the ENTER switch on the AWC Control box. The WEIGHT in light will glow red.
16. Add 2 scoop of LECOCEL accelerator to the crucible.
17. Set the UP/DOWN switch to DOWN on the furnace.
18. Place the loaded crucible on the pedestal.
19. Set the UP/DOWN switch to UP. The analyze cycle will begin when the furnace is dosed.

20. Observe the BURN light on the Determinator.

21. When the Carbon and Sulfur READ lights glow red record the values displayed on the DVM-s.

22. Set the UP/DOWN switch to DOWN and remove the hot crucible with tongs.

Return to step 12.

While the sample is burning _ second sample may be weighed on the EB-25.

It is recommended to calibrate the values evry day by using alumina (or steel) standards.

CALCULATION

It is expedient to make 5 parallel determinations and to calculate the average values.

PRECISION

The variation coefficient for the carbon content of alumina is 5, for sulfur is 10.

TIME CONSUMPTION

One simultaneous determination is finished in one minute. It is expedient to make 5.

20. X-RAY SPECTROMETRY AND AUTOMATIC BAUXITE ANALYSIS BY NEUTRON ACTIVATION

X-RAY FLUORESCENCE ANALYSIS OF BAUXITE SAMPLES

The principle of the X-ray fluorescence analysis is the following: the elements of the materials are excited to emit their characteristic radiation. By measurement of the wavelength of the emitted characteristic radiation the elements present in the sample can be identified and the measured intensities are proportional to the concentration of the respective elements.

THE PURPOSES OF THE EXERCISE

1. Preparation and measurement of the intensities of 3 bauxite samples by means of a Philips PW 1540 vacuum spectrograph.
2. Concentration evaluation with a HP 9830 desk calculator

SHORT DESCRIPTION OF THE INSTRUMENT TO BE USED IN THE EXERCISE

Fig. 8.34.represents the arrangement and working principle of a conventional spectrometer like ours. A spectrometer consists basically of a system of slits or collimators and monochromator, the analysing crystal in our case.

Excitation: X-ray tubes with various anodes (W, Mo, Au, Ag, Rh, Cr) are available. Choice may be made according to the elements to be determined. Depending on the composition of the sample, the excited spectrum will consist of characteristic lines of different wavelengths. Table 8.12. To isolate a selected wavelength, an appropriate analysing crystal is used.

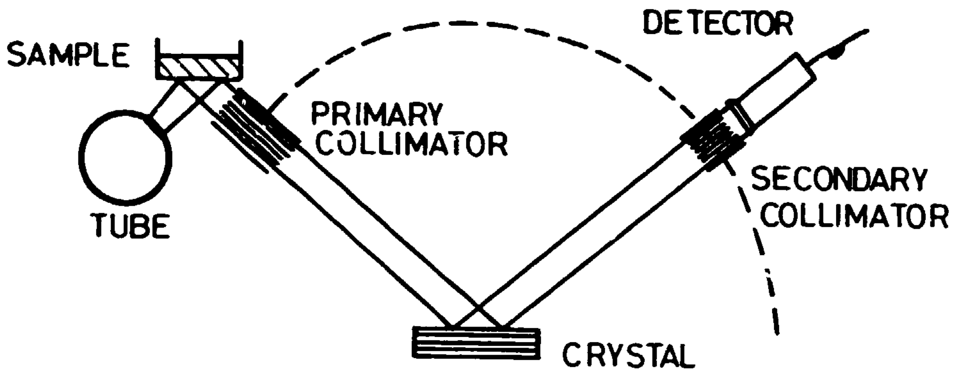


Fig.8. 34

PLANE CRYSTAL SPECTROMETER GEOMETRY

Dispersion of the radiation: A portion of the excited radiation passes through a primary collimator. The purpose of the collimation is to limit the divergence of the X-ray beam. The collimator system consists of parallel plates with given distances (160-500 µm). The selection of the optimum collimator must be made taking into account the dispersion of the analysing crystal employed. From the primary collimator the parallel beam is allowed to fall into the surface of a single crystal. Here the radiation is diffracted in accordance with the Bragg-relationship:

$$n \quad = 2d.\sin\theta$$

After diffraction, the radiation passes through a secondary collimator to the detector. In order to disperse successfully the radiation in the 0.2-26 Å (0.02 nm-2.6 nm) range, it is necessary that a suitable d-value analysing crystal be available, with consideration to the angular range over which the spectrometer will function. The upper limit of the spectrometer is normally fixed by the angle at which further movement of the detector system is prevented by the presence of the sample chamber. The magnitude of this particular angle will depend upon the particular spectrometer design but generally it is about 145° (2). The lower limit is set by the angle at which the analysing crystal no longer intercepts the majority of the incident radiation. The dispersion of the analysing crystal can be derived from the Bragg equation. The longest possible wavelength that can be dispersed with a given crystal is limited to $\lambda = 2d$ but in most cases it is only $\lambda = 1.6d$ (due to technical reasons). Table 8.13 shows the data of the most commonly used analysing crystals.

Detection: The most widely used detectors in X-ray spectrometry are the scintillation counter and the flow proportional counter. The scintillation counter is used for the detection of shorter wavelength (0.02 nm-0.25 nm) while

Table 8.12.

EXCITATION ENERGIES IN kV-s

Element	Atomic number	K series kV	L series kV	M series kV	N series kV
Mg	12	1.30			
Al	13	1.55			
Si	14	1.83			
Ca	20	4.03			
Ti	22	4.95			
Cr	24	5.98			
Fe	26	7.10			
Cu	29	8.86			
Mo	42	20.00	2.87	0.51	0.06
Ag	47	25.5	3.79	0.72	0.10
W	74	69.3	12.1	2.81	0.59
Au	79	80.5	14.4	3.43	0.79
Pb	82	87.6	15.8	3.85	0.89

Table 8.13.

ANALYSING CRYSTALS

Crystal	Reflection Plane	2d spacing Å	Wavelength region Å	Detectable atoms K series	Detectable atoms L series
Lithium Fluoride	(200)	4.028	0.2-3.8	K - Ag	In - U
Penta erythritol	(002)	8.742	3.3-9.0	Al - Ca	Rb - Sb
Potassium Hydrogen Phtalate (KAP)	(1011)	26.4	9.0-26.0	O, F, Na, Mg	V - As

for the detection of the longer wavelength (0.15 nm-2.6 nm) flow counters are applied. Their great advantage is the short dead time (0.02-0.2 usec) and that the mean pulse amplitude is directly proportional to the energy of the incident X-ray photon. Their proportionality allows the elimination of unwanted pulses by use of energy discrimination methods in the form of pulse height selection. Application of pulse height selection methods gives considerable improvement in peak to back-ground ratio too.

SEQUENCE OF THE EXERCISE

1. Preparation of samples: For the X-ray fluorescence spectometric measurements the sample must be prepared into a suitable form. This depends on the sample material (metal, alloy, oxide, ore etc.) and on the order of magnitude of the element to be determined. The sample peraparation consists of bead-fusion from fine powder (60 μm). By diluting and fusing the samples with the flux material the so called matrix effects are eliminated or reduced considerably. In case of bauxites, 0.3 g of the previously ignited and ground bauxite are weighed in after determination of the ignition loss, then the bauxite is fused with sodium tetraborate at a temperature of 1050-1100 ^{o}C. The weigth of the finished bead should be about 3.4 g. The fusion takes place in platinum crucibles alloyed with 5 % gold. The advantage of this alloy is that the melt does notwet the walls of the crucibles and the beads can be removed from them without any loss. Beads are fused either with electric (preferable high frequency) furnaces or with gas burners. When working with gas burners, care must be taken for not to damage the platinum crucibles: always heat them in oxidizing flame, never let them get into the reducing area of the flame. After melting the beads are cooled rapidly to room temperature. Standards are prepared in the same way.

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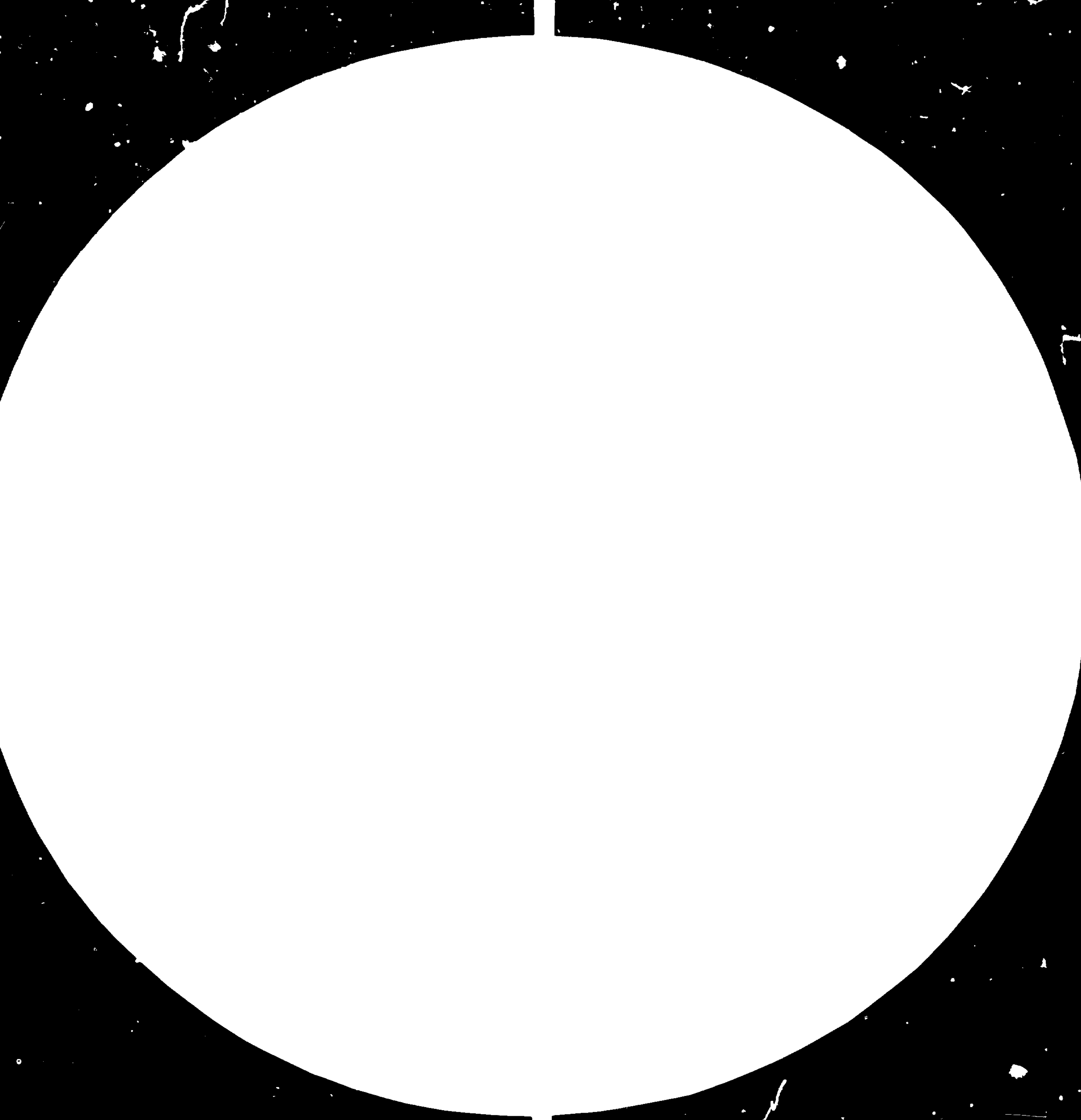

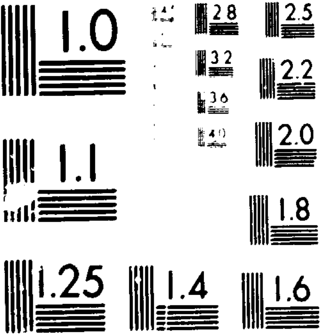

MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

2. Measurement of the intensities in a Philips PW 1540 vacuum spectrograph equipped with automatic sample changer.

a) Switching on: water cooling, high voltage generator, compressed air to the pneumatic sample changer, electronical units.

b) Setting of the parameters according to Table 8.14., starting the teletype for printing and punching.

EVALUATION OF DATA

As X-ray spectrometry is not an absolute analytical method, the measured intensities can be converted into concentration values only by relating them to measurements on standards. The standard may be an accurately analysed sample or an artifical one (weighed in of pure oxides). The best choice of the standard is when its composition is very near to that of the samples to be analysed. In this case the intensity values are converted to concentration values by a simple proportionality:

$$C_x = \frac{R_x}{R_{st}} \cdot C_{st}$$

where:

C_x : concentration of element in sample
R_x : count rate of element in sample
C_{st} : concentration of the same element in the standard
R_{st} : count rate of the same element in the standard

When analyses of a series of samples are performed where more or minor deviations from the standard compositon may occur, corrections for interelement effects are necessary. In this case, too, actual analyses are carried out by using the ratio (unknown/standard) method, and then calculating

Table 8.14.

EXEMPLARY CHART FOR SETTING THE PARAMETERS

Element	Line	Anode	kV/mA[a]	Collimator[b]	Crystal	Detector	Measuring time
Al	Kα	Cr	40/24	C	PE	Fl.C.	40 s
Si	Kα	Cr	40/24	C	PE	Fl.C.	100 s
Ca	Kα	Cr	40/24	F	LiF	Fl.C.	60 s
Ti	Kα	Cr	40/24	F	LiF	Fl.C.	20 s
Fe	Kα	Cr	40/24	F	LiF	Fl.C.	20 s

[a] The power rating of the generator used is limited to 1 kW

[b] F = fine collimator (160 μm);
C = coarse collimator (480 μm)

the concentrations from the usual relationship. But this time coefficients for interelement effect correction are included, in the equations previously determined from a series of measurements. The calculations are carried out by a small program, in which corrections for background and for dead time are also included. (Dead time correction is a built-in program in modern equipments).

$$C_{Fe_2O_3} = \frac{R_x}{R_{st}} \cdot C_{st} \cdot \left[1 + \alpha_{Ti} \cdot \Delta C_{TiO_2} + \alpha_{Ca} \cdot \Delta C_{CaO}\right]$$

$$C_{TiO_2} = \frac{R_x}{R_{st}} \cdot C_{st} \cdot \left[1 - \alpha_{Fe} \cdot \Delta C_{Fe_2O_3} + \alpha_{Ca} \cdot \Delta C_{CaO}\right]$$

$$C_{CaO} = \frac{R_x}{R_{st}} \cdot C_{st} \cdot \left[1 - \alpha_{Fe} \cdot \Delta C_{Fe_2O_3} - \alpha_{Ti} \cdot \Delta C_{TiO_2}\right]$$

$$C_{SiO_2} = \frac{R_x}{R_{st}} \cdot C_{st} \cdot \left[1 + \alpha_{Al} \cdot \Delta C_{Al_2O_3} + \alpha_{Fe} \cdot \Delta C_{Fe_2O_3}\right]$$

$$C_{Al_2O_3} = \frac{R_x}{R_{st}} \cdot C_{st} \cdot \left[1 - \alpha_{Si} \cdot \Delta C_{SiO_2} + \alpha_{Fe} \cdot \Delta C_{Fe_2O_3}\right]$$

where: $\Delta C_{Fe_2O_3} = C_{xFe_2O_3} - C_{stFe_2O_3}$

Summary: (handling in measurement in the prescribed form). At the end of the exercise a short report has to be written containing the concentrations of the main components of the three bauxite samples.

FAST DETERMINATION OF THE SiO_2 AND THE Al_2O_3 CONTENT OF BAUXITE SAMPLES BY NEUTRON ACTIVATION

THEORETICAL INTRODUCTION

Due to the action of fast neutrons, part of the Si atomic nuclei changes into radioactive ^{28}Al atomic nuclei in the course of the following nuclear reaction:

$$^{28}Si^{-}/n,p/^{28}\ Al$$

The activation intensity of the irradiated sample depends on the SiO_2 concentration and the neutron flux. The half life of the radioactive substance is 138 secs. During the radioactive decay of each ^{28}Al atomic nucleus, a beta particle and a photon is released and by this way it transforms into a stabile ^{28}Si automic nucleus. The slow neutrons activate the sample's Al atomic nuclei, through the

$$^{27}Al/n,\ \ /^{28}Al$$

atomic reaction.

Therefore activation in both cases results in the same atomic nuclei, and there is no difference in their radiation either. (Total interference.) The sample's Si and Al content can be determined, if it is irradiated with both types of neutrons and the resulting activity is measured separately. Hungary's Bauxite Industrial Analytical Automat uses a ^{248}Am-Be neutron source to produce the two kinds of radiation. Mostly fast neutrons are available at the centre position of the cylinder shaped neutron source, where the position for activation is situated. The source is surronded by a paraffin moderator, which slows down the neutrons, so here slow neutrons are in majority. In the side activation position therefore a larger portion of ^{28}Al nuclei will be activated as compared to the ^{28}Si nuclei whereas in the previous position this relation is reverse.

The radiation intensity from the activated sample in the first position depends mainly on the number of Si nuclei i.e. the SiO_2 concentration, on the other hand the activation carried out in the second position depends mainly on the Al_2O_3 concentration.

The impulse counts measured in each measuring channel are function of the sample's intensity and the concentration of the contributing substances. The impulse counts measued in the Si channel is given by the following equation:

$$N_{Si} = k_1 \cdot c_{SiO_2} + k_2 \cdot c_{Al_2O_3} \qquad (1)$$

The impulse rate measured in the Al channel is

$$N_{Al} = k_3 \cdot c_{SiO_2} + k_4 \cdot c_{Al_2O_3} \qquad (2)$$

The k_1-k_4 constants stand for the sensitivity of the measurement

- k_1 equals the SiO_2 sensitivity of the Si channel, cpt/% SiO_2,
- k_2 equals the Al_2O_3 sensitivity of the Si channel, cpt/% Al_2O_3,
- k_3 equals the SiO_2 sensitivity of the Al channel, cpt/% SiO_2,
- k_4 equals the Al_2O_3 sensitivity of the Al channel, cpt/% Al_2O_3.

The k contants are characteristic of the equipment used. Their value depends on the activation and measurement geometry, moreover, on the duration of the activation and measurement cycles. After the measurement of the impulse counts, the inverses of equations (1), (2) make possible to determine the sample's Si and Al components:

$$c_{SiC_2} = q_1 \cdot N_{Si} + q_2 \cdot N_{Al} \qquad (3)$$

$$c_{Al_2O_3} = q_3 \cdot N_{Si} + q_4 \cdot N_{Al} \qquad (4)$$

The q_1-q_2 inverse constants have to be determined on the same equipment from the neutronactivation data obtained from standard bauxite samples of known chemical composition.

From mathematical aspects, the NAA measuerment of two standard samples would be enough to calculate the inverse constants from equations (3) and (4), nevertheless, the deviation of chemical analysis and NAA necessitates the use of data from several samples for accurate calibration.

From the measured data the inverse constants are determined by Gauss's least square statistical method so that the deviation of computed data from known chemical analysis would become a minimum.

The SiO_2 and Al_2O_3 concentrations of unknown bauxite samples can be determined from equations (3) and (4), using a calibrated equipment.

THE EQUIPMENT SET-UP

The Bauxite Industrial Analytical Automata delivers the samples closed into polyethylene tubular packages, by pneumatic tube transport into the activation and measuring positions.

From the ground bauxite samples, 2-2 tubes have to be filled with 8.5 gramms of the substance each, by compression. The automata's sample magazine may handle 10 sample pairs simultaneously. The samples are moved about pairwise in a cyclic manner and then measured for component content. Finally the equipment prints hardcopy. To increase the measuring accuracy, the samples may be run several times, resulting parallel measuring data.

The first sample pair on the first forwarding step reaches the X-ray fluorescent measuring position, where the slight γ-radiation of inbuilt radioactive sources, induces the samples to emit fluorescent X-rays (Fig. 8.35.).

In the first measuring position the CaO and TiO_2 concentrations, in the other the Fe_2O_3 concentration can be determined.

During the second cycle the first sample pair is in the γ-transmissional and the neutrontransmissional positions, where radiation abscrption can be measured depending on the composition and on the humidity of the sample, respectively. In the meantime the second sample pair reaches the X-ray fluorescent measuring position.

In the third cycle one of the tubes of the first sample pair reaches the fast neutron activation space, whereas the pair's other tube the slow neutron space, and until the next cycle they are activated according to the above mentioned reaction equations.

In the next step the activated samples are transported to a Geiger-Müller instrument, which measures the radiation intensity during radioactive decay i.e. the impulse rates in accordance with equations (1) and (2).

Finally the tubes are returned into the magazine, but in an inverse order. This way when the process is repeated the tube that has been exposed to fast neutrons, is then exposed to slow neutrons. As a result of the repeated runs, by averaging the data, failures due to sample preparation can be lessened. The equipment after each cycle prints the impulse counts of each channel or, depending on the adjustion, the component concentrations by using equations (3) and (4) and the equipment's mini-computer. Naturally it is necessary in the second case to calibrate the equipment with standards and to include the q_1-1_4 constants into the computing unit through wiring.

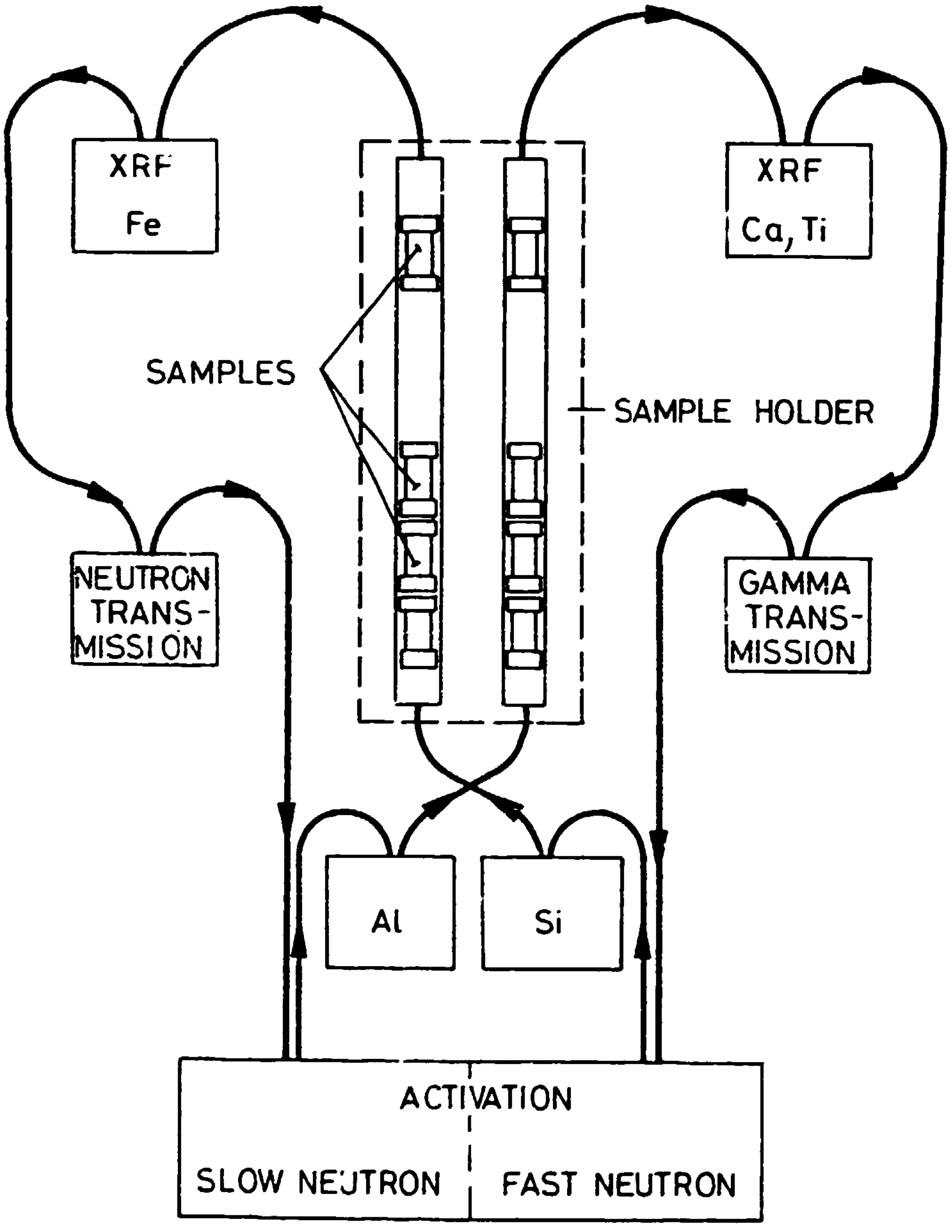

Fig. 8. 35

AUTOMATIC ANALYSER USING NEUTRON ACTIVATION

MEASUREMENT EXERCISE

Those who take this exercise, receive the impulse count data of 10 previously and repeatedly run bauxite samples, in the printed output format of the analytic automata.

1. Calculate the Si and Al channel's average impulse counts for each sample respectively.

2. Determine from the known chemical composition of the first 5 samples and from the impulse counts the q_1-q_2 constants.

3. By using the calculated constants and the samples' average impulse counts calculate from equations (3) and (4) the SiO_2 and Al_2O_3 concentrations of all 10 samples.

4. Produce a table illustrating the deviations of chemical analysis and the computed data, comment on the results. For each component determine the correlation between chemical and NAA analysis.

A preprogrammed mini-calculator is available for the computation.

APPENDIX

Gauss's least square method to minimize error, for two variables

To determine the q_1-q_4 constants we use n sample units. Let a_i, b_i, A_i, B_i be the variables of the i-th bauxite sample, where

a_i - stands for the SiO_2 concentration of i-th sample, in %

b_i - stands for Al_2O_3 concentration of the i-th sample, in %

A_i - stands for the impulse rate of the i-th sample measured in the Si-channel, in cpt

B_i - stands for the measured impulse count of the i-th sample in the Al-channel, in cpt

Due to measurement errors, q_1-q_4 constants to be computed will not be exact, so equations (3) and (4) are not valid. The following equations are to be used, instead:

$$q_1 \cdot A_i + q_2 \cdot B_i - a_i = \alpha_i \qquad (5)$$

$$q_3 \cdot A_i + q_4 \cdot B_i - b_i = \beta i \qquad (6)$$

The α_i, β_i deviations between NAA and chemical analysis would naturally be different for each sample. Gauss's method prescribes to keep the square sums to a minimum

$$\sum_{i=1}^{n} \alpha_i^2 = \left[\alpha\alpha\right] = \text{min, and} \quad \sum_{i=1}^{n} \beta_i^2 = \left[\beta\beta\right] = \text{min.}$$

These two conditions result the following four:

1. $\dfrac{\partial[\alpha\alpha]}{\partial q_1} = 0$
2. $\dfrac{\partial[\alpha\alpha]}{\partial q_2} = 0$
3. $\dfrac{\partial[\beta\beta]}{\partial q_3} = 0$
4. $\dfrac{\partial[\beta\beta]}{\partial q_4} = 0$

By analyzing the 1st condition we find:

$$\frac{\partial[\alpha\alpha]}{\partial q_1} = 2 \sum\left(\alpha_i \frac{\partial \alpha_i}{\partial q_1}\right) = 0$$

so, because $\dfrac{\partial \alpha_i}{\partial q_1} = A_i$

$$1/2 \; \frac{\partial\, \alpha\alpha}{\partial q_1} = \sum\left(\alpha_i \frac{\partial \alpha_i}{\partial q_1}\right) = \sum (q_1 . A_i . a_i + q_2 . A_i . B_i - A_i . a_i) = 0$$

By placing the summation sign before each member und using square brackets, we get:

$$q_1 \cdot [AA] + q_2 \cdot [AB] = [Aa]$$

Simularly expanding the other 3 equations, we get the following four normalized equations, where the variables are the cross products of NAA and chemical analysis date. By solving them the q_1-q_4 constants result.

1. $q_1 \cdot [AA] + q_2 \cdot [AB] = [aA]$
2. $q_1 \cdot [AB] + q_2 \cdot [BB] = [aB]$
3. $q_3 \cdot [AA] + q_4 \cdot [AB] = [bA]$
4. $q_3 \cdot [AB] + q_4 \cdot [BB] = [bB]$

The 1st and 2nd furthermore the 3d and 4th equations are to be solved in the same way as simultaneous equations.

The mini-computer program used during the exercise after feeding in a_i, b_i, A_i, B_i is preprogrammed to do the computing and to print the constants.

21. THERMOMETRIC TITRATIONS FOR THE DETERMINATION OF MAIN COMPONENTS OF ALUMINATE LIQUOR

PRINCIPLE

The caustic soda content (Na_2O) can be titrated with hydrochloric acid titrant. The end point of titration can be indicated by a heat effect due to the different heat of reaction of OH^- and CO_3^{2-} + H_3O^- reactions. ($OH^- + H_3O^- \longrightarrow 2H_2O$ about 14 kcal/mol.) The disturbing effect of precipitated $Al(OH)_3$ can be eliminated by addition of Seignette salt as complexing agent. The Al_2O_3 content can be determined after titration of the Na_2O_c. The tartarate complex of aluminium can be decomposed by addition of potassium fluoride according to the following equation:

$$Al(OH)_3\text{-tartarate} + 6\,F^- \longrightarrow AlF_6^{3-} + 3OH^-$$

The hydroxide ions set free can be titrated as previously.

PROCEDURE

Transfer 10 ml of 1:10 diluted aluminate liquor to a 100 ml beaker containing 20 ml of 25 % Seignette salt solution and a stirrer road, and dilute it with distilled water to 50 ml volume. Take the beaker to the measuring cell of the thermometric titrator, start the stirring and set the sensitivity knob to the "K" position. Set the working point to 16 V and switch on the automatic buret filled with 2 N HCl. At the end point the buret will stop and the consumed volume of the titrant can be read off ($V_{c/ml}$). Give 20 ml of 40 % $KF.2H_2O$ solution to the beaker, set the sensitivity knob to the "A" position and set the working point to 21 V. Start the automatic buret and read the consumed volume of the titrant off when the buret stops (Va μl).

Calibrate for both Na_2O_c and Al_2O_3! Two or three different aluminate liquor samples of known composition are required for the calibrations. The procedure is the same as the previous one.

CALCULATIONS

The result of titrations can be calculated according to the following equation:

$$y = m \cdot x + b$$

where	y	the unknown concentration (Na_2O_c and Al_2O_3, resp.)
	m and b	constants calculated from the calibration experiments (different for Na_2O_c and Al_2O_3, resp.)
	x	consumed volume of titrant (Vc and Va μl, resp.)

A pocket calculator is very useful for the performance of this calculation.

PRECISION

Variation coefficient is 1.

TIME CONSUMPTION

15 minutes in the case of determination of caustic molar ratio.

Note: The caustic molar ratio of red mud and hydrate slurry can be determined without filtration of solid phase. Titre the 1:10 diluted slurry sample according to the previous procedure.

$$k = \frac{Na_2O}{Al_2O_3} \cdot 1.645$$