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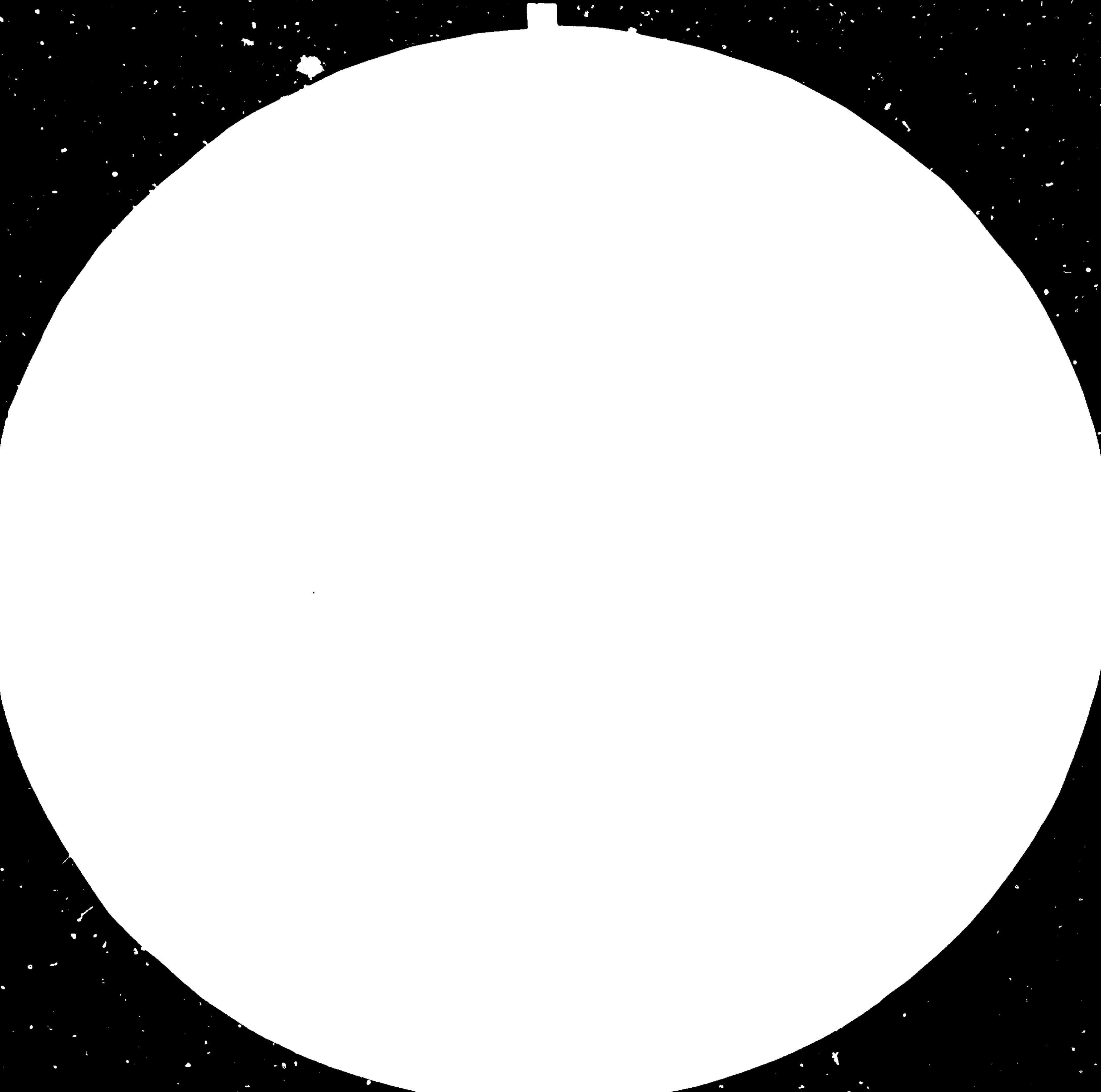
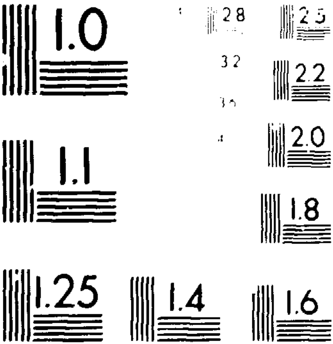
UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org





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United Nations Industrial
Development Organization

Laboratory Practice
in
ALUMINA PRODUCTION

Theoretical Background
and
Laboratory Manual

L. Bottyan

Group Training
ALUTERV-FKI
BUDAPEST, 1983

Theoretical Background and Laboratory Manual

With contribution of

L. Bottyán
A. Csordás
I. Fehér
Gy. Horváth
I. Molnár
Z. Sartowski
L. Tomcsányi
L. Tóth
K. Vékey
Gy. Záray
J. Zöldi

Edited by

L. Bottyán
A. Csordás
T. Turmezey

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

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1. INTRODUCTION

Alumina production, like any other technology, requires evaluation of the raw material, the intermediates and the product.

This evaluation is based on chemical, physico-chemical, mineralogical and morphological analysis as well as tests of technological character. The knowledge of the principle and practice of these methods is essential for alumina technologists.

The objective of this volume is to cover theoretical background of and instructions to laboratory investigations in alumina production.

Theoretical background given in the text as "PRINCIPLES" covers the required basic knowledge for understanding a particular method, with the admitted objective of brushing up and not of comprehension. The second part of the chapters gives "EXPERIMENTAL" details, materials, apparatus, etc., whilst the third one gives detailed "PROCEDURE" to follow carrying out certain experiments. Due to the diversity of the field covered, inspite of the editors best endeavour to keep this structure throughout the text, there are certain deviations from it.

This volume is a revised edition of the Laboratory Manual of a previous joint UNIDO/HUNGALU group training held in Budapest, in 1979.

It is necessary to provide a comprehensive guide to the shorter group training for alumina technologists than that of the one organized in 1979 for people of a wider field of interest. Due the shorter period of time available for laboratory practices, certain investigations cannot be completed, however, candidates are supplied with data of earlier experiments.

For practical reasons, certain tables, forms, graphs, though part of this manual, are filed separately.

We believe, this volume will somewhat contribute to the UNIDO´s noble objective of "promoting the establishment and development of aluminium industries in developing countries by facilitating the transfer and adaptation of technology and the dissemination of technological information".

Editors

2. LABORATORY SAFETY

In compiling the present guide our objective has been to give safety engineering and fire protection information in accordance with the characteristics of the research field of our Institute.

Our Institute is a dangerous plant by nature. The different chemical substances spell danger in addition to the machinery and equipment. These dangers can cause accidents, fire or other harms if they are not known and the different rules are not complied with /technological rules, preventive measures and other safety engineering and fire protection instructions/.

Instructions for fire protection

The characteristics of our Institute bring about fire hazard as well. The inflammability of the substances and solvents used in the experiments and research work is different. Also the rules of the work to be carried out with them are varying accordingly from the point of view of fire protection.

The fire-service should get to know of the cases of fire as soon as possible. An alarm in due time ensures rapid intervention and efficient fire-fighting. Everybody is obliged to report observed fires and even extinguished fires. At our Institute there are a two kinds of fire-alarm: by telephone, dialling 05, the telephone number of the fire service /outside line/, or by calling the porter´s lodge of the Institute /domestic line/. The latter is to be carried out by dialling the number 226 and reporting the following data on the case of fire:

a./ who reports the fire /the name of the caller/,
b./ where did the fire break out /the place of the fire/,
c./ what kind of material is burning,
d./ is there life-danger or not,
e./ what is endangered /a cooling centre or some other plant in the vicinity/.

The fires and burning chemical substances must not be extinguished with water.

The fire extinguishers in the plants, premises and corridors are suitable to extinguish every kind of fire. It must be remembered: they should not be used on a burning man! At our Institute carbon-dioxide, dry chemical and gas extinguishers are used.

The burning person is either placed under an emergency shower and the water is run over him, or is wrapped tightly into an extinguishing blanket and hindered from running. It is expedient to take off burning clothes. After extinguishing the fire, the person must be taken to a doctor.

The extinguishing of solvent fires must always start at the edge of the fire, gradually progressing towards the seat of the fire. In case of fires in closed premises waste gas poisoning and anoxia must be taken into consideration.

Fires of electric origin can be extinguished after cutting off the current. The regularly used fire extinguishers are suitable for extinguishing electric fires.

Rules for laboratories

Rules, instructions and preventive measures must be put into force with a view to prevent accidents, poisoning and fires. The provisions of the preventive measures are obligatory for everybody - staying or working in the area under the ruling of the preventive measure - alike. The most important rules regarding to laboratories will be surveyed as follows:

only the persons attached to the laboratories as well as the persons entitled to supervision may stay in the laboratories, etc. for running the job. Unauthorized persons are forbidden to stay there. After working hours nobody may remain there - except if he is particularly given orders to do so by the leader of the laboratory. A single person may never work alone in a laboratory. Those workers may be assigned to laboratory work who know all the peculiarities of the laboratory in question: the labour processes carried out there, the equipment, the place of water, steam, gas, and electric disconnectors, emergency ventilation and lighting switches and can intervene in case of need, i.e. can operate /turn on and off/ them, they know the fire alarm and other alarm devices, they know how to use manual extinguishers and can act with the necessary competence in case of fire, accident.

It is essential that the means for alleviating the consequences of the accidents that had taken place be at hand. The first-aid box should always be filled with materials necessary for first aid and there should be an expert voluntary ambulance worker in the laboratory. Eye-baths must be introduced: in case of acid getting into the eye it must be bathed in a 2 per cent solution of sodium bicarbonate, if it is an alkali, a 2 per cent solution of boric or acetic acid must be used.

Gas cylinders may be stored in standing, fixed position only.

Meals may be taken only in the appointed place, after a thorough handwash.

Smoking is permitted in the laboratory, but the permission is granted or withdrawn by the leader of the laboratory. To smoke with one´s hands stained with chemicals spells poisoning danger. Laboratory instruments and chemicals may not be used for taking one´s meals. No food may be stored in the refrigerator together with chemical substances.

The chemical substances used for washing laboratory vessels and laboratory instruments and materials remaining as waste in the course of work in general /acids, alkalis, alcohols, other solvents, etc./ may not the discharged into the sink. They must be passed down for destruction in well-closed vessels regularly used for this purpose, taking into consideration their chemical interaction. Namely the solvents getting into the canal will evaporate, their fumes may cause canal explosions, and acidic and alkali materials may destroy the sewerage system.

It is strictly forbidden to wear clothes made of synthetic fibres in laboratories where there are highly inflammable and explosive materials, solvents in use. Namely these clothes are subject to static electricity and in motion this electricity causes constant sparking.

It is forbidden to fit together wires and cords domestically or operate electric motors unearthed. Every worker in the laboratory should know the personal protective wear introduced there /face-guard, safety goggles, industrial and household rubber gloves, PVC and rubber aprons, gas masks/ and is obliged to use them if it is necessary in running the job.

After hours every disconnector must be turned on, which must be supervised by the leader of the laboratory or a person assigned to this job. After hours nothing which might cause a fire or an accident may be left in the laboratory. The laboratory must be closed after hours - even in the daytime - so that no unauthorized person can enter it.

3. CHEMICAL ANALYSIS OF BAUXITE AND ALUMINATE LIQUORS

Introductory notes

Analysis for the alumina industry involves determinations of the main components, accompanying components and impurities.

This chapter gives the basic methods in the analysis of bauxite and aluminate liquors. Due to the diversity of the field, the structure of this chapter is somewhat different from the rest of the Manual. The text is divided into Methods containing paragraphs such as "Principle", "Apparatus", "Reagents", "Procedure" and "Calculation".

Method 1 describes the preparation of commonly used reagent solutions. Solid reagents are not listed there, although they are referred to wherever it is necessary to use them.

In Method 1 as well as in the analytical methods,

- water means distilled water,
- hot water means water of about 70°C,
- all reagents are to be of analytical or higher purity,
- weighing means weighing on an analytical balance /unless otherwise stated/,
- volumes of liquids are to be measured by means of a graduated cylinder, unless otherwise stated,
- items commonly used in any chemical laboratory may sometimes be omitted from the lists under "Apparatus",
- in accordance with the SI system, <u>M</u> stands for concentration /mole/dm^3/ and <u>mole</u> stands for the amount of the substance.

METHOD 1 - PREPARATION OF COMMONLY USED REAGENTS

In the following Methods, from Method 4 on, you always find a list of reagents. Their preparation is described in this Method.

List of reagents

The table below shows the list of analytical reagents and indicates the Method in which they are required.

Table 1.

Reagent	Methods	Preparation No.
Triacid mixture	4	1
Sulphuric acid, 9 M	4, 5, 6	2
Potassium permanganate, 2 %	6	3
Mercuric chloride, 5 %	5, 6	4
Phosphorous acid, 20 %	5, 6	5
Sulphuric acid, 0.5 M	6	6
Diphenylamine sulphonic acid sodium salt /sodium diphenylamine sulphonate/	5, 6	7
Potassium dichromate titrant, 0.00833 M	5, 6	8
Stannous chloride solution, 5 %	5, 6	9
Sodium hydroxide solution, 10 M	7	10
Hydrogen peroxide, 3 %	7	11
Ethylene diamine tetraacetic acid disodium salt titrant, /EDTA/, 0.12 M	7, 9	12

Reagent	Methods	Preparation No.
Hydrochloric acid 6 M	7, 9	13
Phenolphtalein, alcoholic indicator solution	7, 8	14
Xilenol orange indicator solution	7, 9	15
Sodium acetate - acetic acid buffer solution, pH 5.5	7	16
Zinc acetate or zinc sulphate titrant, 0.05 M	7	17
Hydrochloric acid titrant, 0.1291 M	8	18
Sodium-potassium-tartrate /Na-K-tartrate/ solution, 25 %	8	19
Barium chloride solution, 20 %	8	20
Zinc acetate titrant, 0.07843 M	9	21
Ammonium acetate - acetic acid buffer solution, pH 5.5	9	22

To help guidance the reverse table below gives the serial numbers of preparation methods.

Table 2.

Analytical method	Preparation of reagent
4	1, 2
5	2, 4, 5, 7, 8, 9
6	2, 3, 4, 5, 6, 7, 8, 9
7	10, 11, 12, 13, 14, 15, 16, 17
8	14, 18, 19, 20
9	12, 13, 15, 21, 22

Procedure

No. 1. Triacid mixture

Note: Mix the components in the order given, and make the additions slowly, while stirring. For no reason should the order given here be changed.

H_2O	485 cm^3
H_2SO_4	115 cm^3 /conc., 96 %, 1.83 g/cm^3/
HCl	200 cm^3 /conc., 38 %, 1.19 g/cm^3/
HNO_3	200 cm^3 /conc., 68 %, 1,42 g/cm^3/

No. 2. Sulphuric acid, 9 M

Note: It should be remembered that the acid should be poured into the water, not the water into the acid.

Pour 500 cm^3 of conc. sulphuric acid into 500 cm^3 of water slowly, with constant stirring. Cool and dilute to 1000 cm^3 with water.

No. 3. Potassium permanganate solution, 2 %

Weigh 20,0 g potassium permanganate. Dissolve it in about 800 cm^3 of water. Make up to 1000 cm^3.

No. 4. Mercuric chloride solution, 5 %

Weigh 50 g $HgCl_2$. Add 10 cm^3 of conc. HCl, and dilute to 1000 cm^3.

No. 5. o-Phosphoric acid, 20 %

Pour 125 cm^3 of conc. phosphoric acid /85 %/ into 500 cm^3 of water and dilute to 1000 cm^3 with water.

No. 6. Sulphuric acid, 0,5 M

Note: It should be remembered that the acid should be poured into the water, not the water into the acid.

Pour 28 cm^3 of conc. H_2SO_4 into about 600 cm^3 of water, slowly, with constant stirring, and dilute to 1000 cm^3.

No. 7. Diphenylamine sulphonic acid sodium salt /sodium diphenylamine sulphonate/ indicator solution, 0,1 %

Dissolve 0.1 g in 100 cm^3 of water, heating gently if necessary. Filter if the solution is not clear.

No. 8. Potassium dichromate titrant, 0.00833 M

Dry a sufficient amount of finely powdered potassium dichromate for 2 hours at 140°C. Cool in a desiccator. Of this dry material weigh 2.4517 g, dissolve in hot water in a beaker, cool and transfer to a 1000 cm^3 volumetric flask. Make up to the mark at 20°C.

Note: Potassium dichromate is a primary standard. It is desirable to make its solution so that it will be exactly right without any adjustment.

1 cm^3 of 0.00833 M $K_2Cr_2O_7$ solution represents 0.003992 g of Fe_2O_3.

No. 9. Stannous chloride solution, 5 %

Dissolve 55.2 g of $SnCl_2.2H_2O$ in 500 cm^3 of 6 M HCl and dilute to 1000 cm^3 with water.

This solution can be kept for two weeks.

No.10. Sodium hydroxide solution, 10 M

Note: Use rubber gloves and protective goggles when preparing this solution.

Dissolve 410 g of sodium hydroxide in 590 cm^3 of water, cool, make up to 1000 cm^3 with water,

No.11. Hydrogen peroxide 3 %

Dilute 100 cm^3 of concentrated /30 %/ hydrogen peroxide to 1000 cm^3 with water.

No.12. Ethylene diamine tetraacetic acid disodium salt /EDTA/ titrant, 0.12 M

Dissolve 45.0 g of ethylene diamine tetraacetic acid disodium salt dihydrate in a beaker in 750 cm^3 of water. Transfer to a 1000 cm^3 volumetric flask and make up to the mark with water.

Keep the solution in a polyethylene container.

Note: This solution is not standardized because a blank is always made.

No.13. Hydrochloric acid 6 M

Note: It should be remembered that the acid should be poured into the water, not the water into the acid.

Pour 500 cm^3 of conc. /38 %/ HCl into 300 cm^3 of water. Cool and dilute to 1000 cm^3 with water.

No.14. Phenolphtalein alcoholic indicator solution /1 %/

Dissolve 5.0 g in 300 cm^3 ethyl alcohol and dilute to 500 cm^3 with water.

No.15. Xilenol orange indicator solution /0,1 %/

Dissolve 0.10 g in 100 cm^3 of water.

No.16. Sodium acetate - acetic acid buffer solution, pH 5.5

Dissolve 408 g $CH_3COONa.3H_2O$ and 32 cm^3 of conc. /96 %/ acetic acid with water to 1000 cm^3.
Set the pH of the solution to 5.5 by adding NaOH or acetic acid.
For a control, dilute one cm^3 of the buffer solution to 15 cm^3 with water and take the pH value.

No.17. Zinc acetate or zinc sulphate titrant, 0.05 M

Weigh 10.98 g of $Zn/CH_3COO/_2.2H_2O$ or 14.38 g of $ZnSO_4.7H_2O$ into an 1000 cm^3 volumetric flask. Pour 10 cm^3 of sodium acetate - acetic acid buffer solution /prepn. No.16/ into the flask and make up to the mark with water.

Standardize the solution to Al_2O_3 standard solution as described below.

Preparation of the standard Al_2O_3 solution

Weigh 2.1170 g of 99.99 % Al foil and place it in a silver dish. Place the dish in an 1000 cm^3 beaker that contains twenty to thirty cm^3 of water. Add 10 g of NaOH pellets to the dish and pour 30 cm^3 of water to it. Cover both the dish and the beaker with watch glasses. When the dissolution is over, transfer the contents of both the dish and the beaker quantitatively to a 2000 cm^3 volumetric flask. Add 250 cm^3 of 6 M HCl, cool and make up to the mark with water.

One cm^3 of this standard solution contains 2000 mg of Al_2O_3.

For the standardization of the zinc titrant, pipette 50 cm^3 of the standard Al_2O_3 solution into a 300 cm^3 Erlenmeyer flask and pipette 20 cm^3 0.12 M EDTA solution. Shake well, add some drops of phenolphtalein and neutralize with 6 M NH_4OH /preparation of 6 M NH_4OH:500 cm^3 of conc. NH_4OH diluted to 1000 cm^3 with water/ to a pale pink colour. Add 10 cm^3 of sodium acetate - acetic acid buffer, dilute to about 120 cm^3, add some pieces of boiling stone and cover. Boil the content of the flask for five minutes. Cool, add 10 drops of 0.1 % xilenol orange indicator and titrate it with the zinc solution to be standardized to a violet red colour /V/.

Make a blank with 20.00 cm^3 of 0,12 M EDTA /pipette!/, adding 100 cm^3 1 M NaCl and 10 cm^3 of sodium acetate - acetic acid buffer solution. Add 10 drops of 0.1 % xilenol orange indicator and titrate it with the zinc-solution to be standardized /V_o/.

One cm^3 of the zinc acetate /sulphate/ solution represents t g of Al_2O_3, t is calculated by the formula:

$$t = \frac{V_o - V}{10000}$$

V_o - blank value,
V - burette reading.

No.18. Hydrochloric acid titrant, 0.1291 M

Dilute 14-15 cm^3 of conc. HCl /38 %/ to 1000 cm^3 with water. Standardize this solution to a $KHCO_3$ solution.

Preparation of the $KHCO_3$ standard solution

Weigh 12.931 g of $KHCO_3$ and dissolve it to 1000 cm^3 in a volumetric flask.

Pipette 25 cm^3 of the $KHCO_3$ solution into a flask. Add some drops of methyl red - methylene blue indicator mixture and titrate it with the HCl solution to a greyish green colour. Add some pieces of boiling stone to the solution, boil for 2 minutes and cool. Repeat titration, boiling and cooling. Titrate the solution to a violet colour. Boil again to check whether the solution gets green again. Repeat titration to a permanent violet colour.

Dilute the HCl solution according to the results. Standardize the diluted solution as described before, with three parallel titrations. The tolerance is ± 0.025 cm^3.

No.19. Sodium potassium tartrate /Na-K-tartrate/ solution, 25 %

Dissolve 1000 g of the salt /$KNaC_4H_4O_6.4H_2O$/ to 4000 cm^3 with water. Filter if necessary. This solution is generally neutral to phenolphtalein. If not, neutralize with HCl or NaOH.

No.20. Barium chloride solution, 20 %

Dissolve 1000 g of $BaCl_2.2H_2O$ to 5000 cm^3 with water. Filter if necessary.

No.21. Zinc acetate titrant, 0.0784 M

Weigh 175 g of $Zn/CH_3COO/_2.2H_2O$ on a general laboratory balance. Add 250 cm^3 of ammonium acetate buffer /see No.22./ and dilute to 10 litres. This solution is slightly more concentrated than necessary. It has to be standardized and diluted properly.
For the standardization, pipette 50 cm^3 of the Al_2O_3 standard solution /see No.17./ and 25 cm^3 of 0.12 M EDTA /see No.12/ into an Erlenmeyer flask, add some drops of phenolphtalein and neutralize with 6 M NH_4OH /see No.17./ to a slight pink colour. Add some pieces of boiling stone and boil gently for 3 minutes. Cool, add 2 drops of xilenol orange indicator and titrate with the zinc acetate solution

to be standardized to a cyclamen colour /V/. Make a blank with 25 cm^3 EDTA /pipette!/ alone /V_0/. The zinc-acetate titrant is 25 /V_0-V/ times more concentrated than necessary. Dilute properly and standardize again. The tolerance is ± 0,05 cm^3.

No.22. Ammonium acetate - acetic acid buffer solution, pH 5.5

Dissolve 300 g ammonium acetate in 700 cm^3 of water. Add 50 cm^3 of conc. acetic acid and dilute to 1000 cm^3. Set and control the pH /5.5/ as described in No.16.

METHOD 2 - DETERMINATION OF MOISTURE IN AIR-DRIED BAUXITE SAMPLES

Principle

The bauxite sample is dried at 130°C for 3 hours. The loss of weight, expressed in weight percents, represents moisture.

Apparatus

Weighing bottle,
Analytical balance,
Oven,
Desiccator with silica gel.

Procedure

Cover the weighing bottle loosely and dry it in the oven at 130°C for 30 minutes. Cover, and cool in the desiccator over blue silica gel for 15 minutes. Put the weighing bottle close to the balance for 20 minutes, open its cover for a second, and weigh it on the analytical balance /T/. Put 2-3 g bauxite in the bottle, cover and weigh /B/.

Cover the weighing bottle loosely and dry it in the oven at 130°C for at least 3 hours.

Cover, and cool in the desiccator for 15 minutes.

Put the weighing bottle close to the balance for 20 minutes, open its cover for a second, and weigh it on the analytical balance /C/.

Calculation

$$\% \text{ Moisture} = 100 \cdot \frac{B - C}{B - T}$$

T - weight of the empty bottle /g/,
B - weight of the bottle with the sample before drying,
C - weight of the bottle and the sample after drying.

METHOD 3 - DETERMINATION OF LOSS ON IGNITION OF BAUXITE

Principle

Mineral components of bauxite form stable compounds at 1100°C. The resulting loss of weight, minus moisture, represents the loss on ignition.

Apparatus

Platinum crucible and cover,
Electric muffle furnace,
Analytical balance,
Desiccator with silica gel.

Procedure

Ignite the platinum crucible and the cover at 1100°C for 10 minutes. Remove the covered crucible from the furnace and cool in the desiccator for 10 minutes. Weigh the crucible on the analytical balance /T/.

Weigh 1-2 g of the dry bauxite sample into the crucible /B/, replace the cover and place it in the furnace. Heat carefully at 400-450°C for 10 minutes, then ignite at 1100°C for 2 hours.

Transfer the crucible to the desiccator, cool for 20 minutes and weigh quickly /C/.

Calculation

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

T - weight of the empty crucible /g/,
B - weight of the crucible and the sample before ignition /g/,
C - weight of the crucible and the sample after ignition /g/,
H - moisture of the air-dried bauxite sample /see Method 2/ /g/.

METHOD 4 - DETERMINATION OF TOTAL SILICA IN BAUXITE AFTER ACIDIC DIGESTION

Principle

Bauxite is dissolved in a mixture of hydrochloric, nitric and sulphuric acid. After completion of the dissolution the SiO_2 content of the sample will be left undissolved in the form of silica gel. The mixture is then filtrated and the filtrate laid aside for further determinations. The precipitate is washed and ignited at 1100°C. The resulting SiO_2 is contaminated with other oxides. The ignited precipitate is evaporated, in the presence of sulphuric acid, with hydrogen fluoride. The residue is also ignited. The loss of weight represents the correct amount of silica in the sample.

Apparatus

Beaker, capacity: 400 cm^3,
Volumetric flask, capacity: 500 cm^3,
Analytical funnel,
Filter paper, medium speed,
Platinum crucible,
Muffle furnace,
Desiccator,
Graduated cylinder, capacity: 100 cm^3,
Washing bottle, polyethylene,
Electric heater,
Sand bath,
Bunsen burner.

Reagents

For the preparation of these reagents see Method 1.

Triacid mixture ,
Sulphuric acid, 9 M ,
Hydrogen fluoride, conc. ,
Potassium pyrosulphate, solid /$K_2S_2O_7$/.

Procedure

Weigh 0.9 - 1.1 g of air-dried bauxite sample on an analytical balance and place in the 400 cm^3 beaker. Wet the sample with about 10 cm^3 of water and add 80 cm^3 of triacid mixture. Cover the beaker with a watch-glass, heat it on an electric hot plate until sulphuric acid fumes are given off. Remove the cover, continue heating on a sand bath to dryness.

Allow it to cool, then add 20 cm^3 of conc. hydrochloric acid and 50 cm^3 of water to the beaker. Heat it on the electric heater until all the salts are dissolved, leaving only the silica gel undissolved. Filter the solution through a medium speed filter paper into a 500 cm^3 volumetric flask. Wash the precipitate with 300 cm^3 of boiling water /acidic stock solution/.

Transfer the precipitate, together with the filter paper, into a platinum crucible. Burn the paper, then ignite the crucible at 1000°C for 60 minutes. Remove the crucible from the furnace, allow to cool in a desiccator for 15 minutes, and weigh /A/. Add 5-6 drops of 9 M sulphuric acid and 8 cm^3 of conc. hydrogen fluoride and carefully evaporate to dryness. Ignite the residue at 1000°C for 10 minutes, transfer the crucible to the desiccator, allow to cool for 15 minutes and weigh /B/.

After weighing, fuse the residue with 3 g of potassium pyrosulphate on a Bunsen burner. Allow the melt to cool, then dissolve it with about 100 cm^3 of the acidic stock solution. Transfer this solution quantitatively to the volumetric flask. Make up to the mark and lay the resulting solution aside for the determination of Al_2O_3, TiO_2 and Fe_2O_3.

Calculation

$$\% \text{ Silica} = \frac{/A-B/ \cdot 100}{G - H}$$

A - weight of the crucible and the precipitate /g/,
B - weight of the crucible and the evaporation residue /g/,
G - weight of the air-dried bauxite sample /g/,
H - moisture of the air-dried bauxite sample /g/ /see Method 2/.

METHOD 5 - DETERMINATION OF TOTAL IRON OXIDE IN BAUXITE

Principle

Iron is determined oxidimetrically with potassium dichromate, after reduction with $SnCl_2$, in the acidic stock solution described in Method 4.

Apparatus

Pipette, capacity: 200 cm^3,
Erlenmeyer flask, capacity: 500 cm^3,
Burette, capacity: 50 cm^3.

Reagents

For the preparation of these reagents see Method 1.

Sulphuric acid, 9 M,
Hydrochloric acid, conc. /sp. g.: 1.19 g/cm^3/,
Mercuric chloride solution, 5 %,
Phosphoric acid, 20 %,
Diphenyl amine sulphonic acid sodium salt, indicator, 0,2 %,
Potassium dichromate titrating solution, 0.00833 M,
Stannous chloride solution, 5 %.

Procedure

Pipette 200 cm^3 of the acidic stock solution /see Method 4/ into a 500 cm^3 Erlenmeyer flask. Put some glass beads in the flask and evaporate half of the liquid. Add 15 cm^3 of cc. HCl and 10 cm^3 of 9 M H_2SO_4.

Boil the solution and reduce the iron in it by the dropwise addition of stannous chloride solution to the disappearance of the yellow colour. Add 2 drops excess.

Cool quickly, add 20 cm^3 of 5 % $HgCl_2$ solution with a quick movement. Wait one minute, then add 20 cm^3 of 20 % H_3PO_4.

Add 2-3 drops of sodium diphenyl amine sulphonate indicator, and titrate immediately with 0.00833 M potassium dichromate solution to a violet colour.

Calculation

$$\% \ Fe_2O_3 = \frac{2.5 \times V \times 0.003992}{G-H} \times 100$$

V - burette reading /cm^3/,
1 cm^3 of 0.00833 M potassium dichromate solution represents 0.003992 g of Fe_2O_3,
G - weight of the air-dry bauxite sample /see Method 4/ /g/,
H - moisture of the sample /see Method 2/ /g/.

METHOD 6 - DETERMINATION OF TOTAL IRON OXIDE IN BAUXITE /ALTERNATIVE METHOD/

Principle

A bauxite sample is fused with potassium hydroxide. The melt is acidified and oxidized with potassium permanganate. The excess of the permanganate is decomposed with cc. HCl. The iron is reduced by a small excess of $SnCl_2$, and titrated chromatometrically, after an addition of $HgCl_2$ and phosphorous acid. The indicator is diphenylamine sulphonic acid.

Apparatus

Silver dish,
Crucible tong,

Funnel, diameter: 10 cm,
Erlenmeyer flask, capacity: 300 cm^3,
Burette, capacity: 50 cm^3,
Bunsen burner.

Reagents

For the preparation of these reagents see Method 1.

Potassium hydroxide pellets,
Sulphuric acid, 9 M,
Sulphuric acid, 0.5 M,
Potassium permanganate solution, 2 %,
Mercuric chloride solution, 5 %,
Phosphoric acid, 20 %,
Ethyl alcohol, 96 %,
Sodium diphenylamine sulphonate, indicator solution, 0,2 %,
Potassium dichromate titrating solution, 0.00833 M,
Stannous chloride solution, 5 %.

Procedure

Weigh 0.5-0.6 g of air-dry bauxite on an analytical balance and place in a silver dish. Add 7-8 g of potassium hydroxide pellets and 5 cm^3 of ethyl alcohol. Burn the alcohol meanwhile moving the dish round and round. Fuse the content of the dish over the flame of a Bunsen burner. Heat the melt for about 5 minutes. Immerse the bottom of the dish in water to cool. When cold, dissolve the melt in 50 cm^3 of water. Transfer the solution with the precipitate to a 300 cm^3 Erlenmeyer flask. Dissolve the precipitate left in the silver dish with 3x10 cm^3 0.5 M H_2SO_4 and add to the flask.

Add 15 cm^3 of 9 M H_2SO_4 to the flask /avoid loss of material due to bubbling/. Boil the solution and add 2 % potassium permanganate drop by drop to a permanent violet colour. Add 15 cm^3 of conc. HCl, boil again and add drops of 5 % $SnCl_2$ until the yellow colour disappears. Add an excess of two drops.

Cool quickly, add 20 cm^3 of 5 % $HgCl_2$ solution with a quick movement. Wait one minute, then add 20 cm^3 of 20 % H_3PO_4.

Add 2-3 drops of sodium diphenylamine sulphonate indicator, and titrate immediately with 0.00833 M potassium dichromate solution to a violet colour.

Calculation

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

V - burette reading /cm^3/
1 cm^3 of 0.00833 M potassium dichromate solution represents 0.003992 g of Fe_2O_3,
G - weight of the air-dry bauxite sample /see Method 4/ /g/,
H - moisture of the sample /see Method 2/ /g/.

METHOD 7 - DETERMINATION OF ALUMINA IN BAUXITE

Principle

Alumina is separated from an aliquot of the acidic stock solution /see Method 4/ by 10 M NaOH in the form of soluble sodium aluminate. The other oxides /Fe_2O_3, TiO_2 etc./ will form insoluble hydroxide precipitates. Aluminium is determined in the filtrate with EDTA titration. Correction is made for the losses due to adsorption on the surface of the hydroxide precipitates /see table at Calculation/.

Apparatus

Pipette, capacity: 200 cm^3,
Beaker, capacity: 400 cm^3,
Glass funnel,
Analytical funnel,
Volumetric flask, capacity: 250 cm^3,
Support stand with two funnel support rings,
Pipette, capacity: 100 cm^3,
Erlenmeyer flask, capacity: 300 cm^3,
Pipette, capacity: 200 cm^3,
Graduated cylinder, capacity: 25 cm^3 and 100 cm^3.

Reagents

For the preparation of these reagents see Method 1.

Sodium hydroxide solution, 10 M,
Hydrogen peroxide solution, 3 %,
EDTA /ethylene diamine tetraacetic acid disodium salt/
solution, 0.12 M,
Hydrochloric acid, 6 M,
Phenolphtalein, alcoholic solution, 1 %,
Xilenol orange indicator solution, 0.1 %,
Sodium-acetate - acetic acid buffer solution, pH 5.5,
Zinc acetate or zinc sulphate titrating solution, 0.05 M.

Procedure

Pipette 200 cm^3 of the acidic stock solution /see Method 4/ into a 400 cm^3 beaker. Boil the solution. Add 25 cm^3 of 1 M NaOH and 5 cm^3 of 3 % hydrogen peroxide and boil the solution for at least 3 minutes. Cool, transfer the slurry quantitatively into a 250 cm^3 volumetric flask, and make up to the mark.

Filter the slurry into a dry 250 cm^3 volumetric flask, using large pore filter paper and the analytical filter apparatus shown in Fig. 1.

When working with the filter apparatus, observe the following rules.
Set the funnel supporting ring on the stand at a height suitable for the flask that contains the slurry. The rubber disc fitted on the neck of the flask should fit on the edge of the funnel.

Compress the rubber tube fitted on the stem of the funnel with the Hoffman clamp. Shake the flask well. Stop the

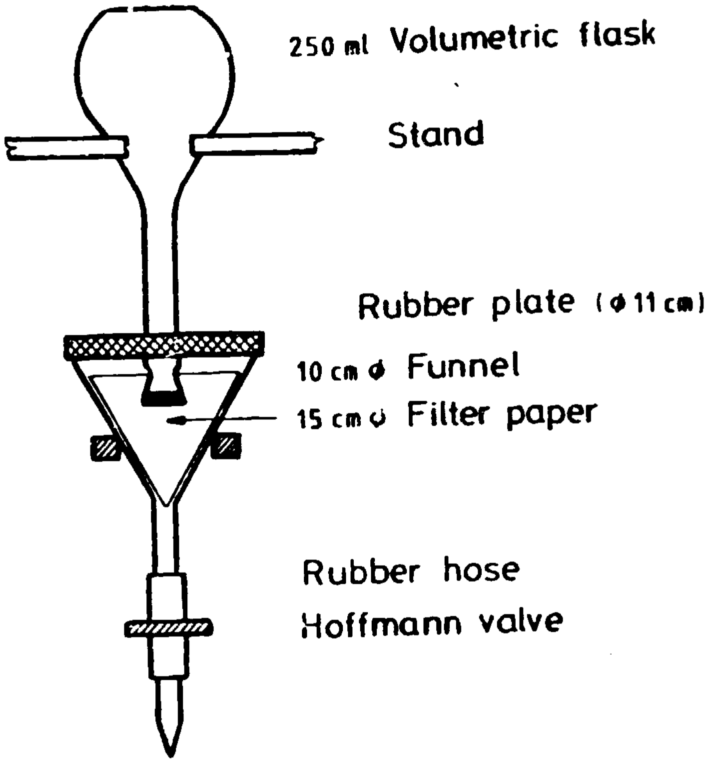

Fig. 1. Analytical filter apparatus

mouth of the flask with a forefinger and set it in the upper support ring. Open the flask and release the Hoffman clamp. The slurry will now fill the funnel to a level defined by the mouth of the flask. This level will automatically be kept throughout the filtration.

When the filtration is over, pipette 100 cm^3 of the filtrate into a 300 cm^3 Erlenmeyer flask. Add 20 cm^3 of 0.12 M EDTA with a pipette. Mix well, then neutralize with 6 M HCl, using phenolphtalein indicator. Add 10 cm^3 of pH 5.5 Na-acetate-acetic acid buffer, several pieces of boiling stones, cover with a watch-glass and boil gently for 5 minutes.

Cool to room temperature, add 10 drops of 0.1 % xilenol orange indicator, and titrate with 0.05 M Zn-acetate to a violet-red colour /V cm^3/.

Make a blank titration daily, according to the following:

Pour 100 cm^3 of 1 M NaCl into a 300 cm^3 Erlenmeyer flask. Pipette 20 cm^3 0.12 M EDTA solution into the flask and add 10 cm^3 of pH 5.5 Na-acetate-acetic acid buffer. Add some drops of xilenol orange indicator and titrate with 0.05 M Zn-acetate solution to a violet-red colour /V_0 cm^3/.

Calculation

$$\% \ Al_2O_3 = 100 \ . \ \frac{/V_0 - V/ \ tx6.25}{G - H}$$

V_o - blank value /cm^3/,
V - burette reading /cm^3/,
t - weight of Al_2O_3 represented by 1 cm^3 of the titrant /for a Zn-solution of 0.0500 M, $t = 0.00255$ g/,
G - weight of the air-dry bauxite sample /see Method 4/,
H - moisture of the sample /see Method 2/.

Note

The amount of Al_2O_3 loss due to adsorption on the surface of the hydroxide precipitates can be estimated on the basis of the Al_2O_3 and Fe_2O_3 content of the sample:

Table 3.

	% Fe_2O_3		
	15	20	25
% Al_2O_3		correction	
45	0,15	0,20	0,25
50	0,15	0,20	0,25
55	0,15	0,20	0,30

Add the proper value to the result of the above calculation.

METHOD 8 - DETERMINATION OF CAUSTIC SODA IN ALUMINATE LIQUORS

Principle

Interfering anions are precipitated with a large excess of barium chloride /CO_3^{2-}, PO_4^{3-}, F^-/, and an aliquot of the clean solution is titrated with HCl for its alkality due to sodium hydroxide and sodium aluminate.

Interference of the aluminium ions is eliminated with the addition of K-Na-tartrate.

Apparatus

Pipettes, capacity: 10, 20, 25, 50 cm^3,
Volumetric flask, capacity: 250 cm^3,
Erlenmeyer flask, capacity: 300 cm^3,
Graduated cylinder, capacity: 25 cm^3.

Reagents

For the preparation of these reagents see Method 1.

Hydrochloric acid titrant, 0.1291 M,
K-Na-tartrate solution, 25 %,
Barium chloride solution, 20 %,
Phenolphtalein indicator solution.

Procedure

Pour about 150 cm^3 of water into a 250 cm^3 volumetric flask. Add 25 cm^3 of barium chloride solution by means of a graduated cylinder and mix well.

Dilute the aluminate liquor sample according to the table given below at Calculation. Pipette 20 or 25 cm^3 of the diluted solution, also according to the table, into the volumetric flask. Make up to the mark with water and stopper with a rubber stopper.

Let the precipitate settle and use the overlaying clean solution for analysis.

Measure 20 cm^3 of 25 % K-Na-tartrate with a graduated cylinder to a 300 cm^3 Erlenmeyer flask. Add 0.5 cm^3 phenolphtalein indicator. Pipette 50 cm^3 of the clean solution into the Erlenmeyer flask. Titrate immediately with 0,1291 M HCl, until the solution is colourless /V/.

Calculation

$$g/dm^3\ Na_2O = \frac{/V + 0{,}06/x4.00}{A}$$

A - volume of the aluminate liquor sample, calculated with respect to the dilution /cm^3/,

V - burette reading /cm^3/

1 cm^3 of 0.1291 M HCl represents 4.00 mg of Na_2O.

Correction for the indicator error: 0.06 cm^3.

Note: In series analysis, samples of the same origin in the process liquor circuit are to be diluted uniformly.

To avoid complications with liquor samples of different concentrations, it is advisable to introduce multiplication factors according to the following table:

Table 4.

Caustic soda g/dm^3	Stock solution cm^3	Dilution cm^3	Multiplication factor, C
300 - 200	25/250	20/250	10
240 - 160	25/250	25/250	8
160 - 50	50/250	20/250	5
50 - 25	10 original/250		2
below 25	20 original/250		1

Introducing the multiplication factor the calculation will be simpler:

$$g/dm^3\ Na_2O_c = /V + 0.06/ \ . \ C$$

METHOD 9 - DETERMINATION OF ALUMINA IN ALUMINATE LIQUORS

Principle

The alumina content of the aluminate liquor sample is taken into EDTA complex with a known amount of EDTA solution. The amount of Al_2O_3 is determined with a back titration of the excess EDTA, using xilenol orange indicator and zinc acetate titrant.

Apparatus

Pipettes, capacity: 10, 20, 25, 50 cm^3,
Volumetric flask, capacity: 250 cm^3,
Erlenmeyer flask, capacity: 300 cm^3,
Electric hot plate,
Graduated cylinder, capacity: 25 cm^3,
Watch-glass.

Reagents

For the preparation of these reagents, see Method 1.

EDTA /ethylene diamine tetraacetic acid disodium salt/ solution, 0.12 M,
Zinc acetate titrant, 0.07843 M,
Xilenol orange indicator solution /0.1 %/,
Ammonium acetate - acetic acid buffer solution, pH 5.5,
Hydrochloric acid, 6 M,
Ammonium hydroxide, 6 M.

Procedure

Dilute the liquor sample the same way and pipette into a 250 cm^3 volumetric flask the same volume as described in Method 8. Acidify with 6 M HCl until all the $Al/OH/_3$ that precipitates at the beginning dissolves. Dilute to the mark with water and pipette 50 cm^3 into a 300 cm^3 Erlenmeyer flask. Pipette 25 cm^3 of 0.12 M EDTA solution into the Erlenmeyer flask. Add some drops of phenolphtalein and neutralize with 6 M ammonium hydroxide to a weak pink colour. Add 25 cm^3 of ammonium acetate - acetic acid buffer and several pieces of boiling stones. Cover with a watch-glass and boil on an electric hot plate for 3-5 minutes.

Cool and titrate the solution, adding 2-3 drops of xilenol orange indicator, with 0.07843 M zinc-acetate to a yellow-cyclamen colour change /V_1/.

Run a blank with 25 cm^3 of 0.12 M EDTA, titrating as described above /V_o/.

Calculation

$$g/dm^3\ Al_2O_3 = \frac{/V_o - V_1/ \times 4.00}{A}$$

A - volume of the aluminate liquor sample, calculated with respect to the dilution /cm^3/,

V_o- blank value /cm^3/,

V_1- burette reading /cm^3/.

1 cm^3 of the 0.07843 M zinc acetate represents 4.00 mg of Al_2O_3.

Note: If the samples are diluted as described in Method 8, the calculation will be simpler:

$$g/dm^3\ Al_2O_3 = /V_o - V_1/.C$$

C - multiplication factor /see Method 8/.

METHOD 10 - DETERMINATION OF CAUSTIC SODA AND ALUMINA IN THE SAME ALUMINA LIQUOR SAMPLE

Note: With the addition of this Method to the list of classical ones our aim was to demonstrate the possibilities which a fast and up-to-date instrumental method can provide in the everyday work of an analytical laboratory. The adaptability of this Method will depend on the domestic possibilities of the user.

Principle

Thermometric titration is an instrumental method to detect the end point of the titration reaction.
The sign to stop titration comes from monitoring the velocity of the change in cell temperature, which necessarily occurs at the end point. For a detailed view consult the Instructions Manual.

Determination of caustic soda

Caustic soda - that is, the total alkality due to the NaOH and $Na/Al/OH/_4$ content of the sample - is determined by titrating with hydrochloric acid. The interference of Al_2O_3 is eliminated with the addition of alkali tartrates prior to the titration. The carbonate ions will not interfere, because their heat of neutralization is cosiderably lower than that of the OH^--ions. Consequently, the burette stops at the end point of the OH^--neutralization.

$$OH^- + H^+ = H_2O \qquad 56.8\ kJ\ /13.6\ kcal/$$
$$CO_3^{2-} + H^+ = HCO_3^- \qquad 5.3\ kJ\ /1.5\ kcal/$$

Determination of Al_2O_3

When the titration of caustic soda is over, fluoride is added to the solution. Fluoride ions liberate hydroxyl ions from the tartrate complex:

$$Al/OH/_3.TAR_x + 6F^- = AlF_6^{3-} + 3OH^- + x.TAR$$

The OH^--ions can be titrated with hydrochloric acid.

Apparatus

Thermatic titrator,
Pipettes, capacity: 5, 10, 20 cm^3,
Volumetric flask, capacity: 100 cm^3.

Reagents

Hydrochloric acid titrant, 2 M, standardized to $KHCO_3$
Sodium-potassium-tartrate.$4H_2O$, 360 g salt dissolved to 1000 cm^3. Density: 1.161 g/cm^3.
$KF.2H_2O$, 517 g dissolved to 1000 cm^3. Density: 1.244 c/cm^3.

Procedure

Cool the sample of alumina liquor to room temperature. Dilute and pipette an aliquot into a titration cell according to the following table:

Table 5.

Na_2O_{caust} g/l	Dilution	Volume taken from the stock solution cm^3	Volume taken from the original solution cm^3	Analyzed ~~v~~olume of the original solution cm^3
300-100	1:10	10	-	1
100-50	1:10	20	-	2
50-20	-	-	5	5
20-10	-	-	10	10
below 10	-	-	20	20

Add 20 cm^3 of K-Na-tartrate into the cell. Make up to the 40 cm^3 mark of the cell with water.
Set the sensitivity of the titrator to level 3 by pushing the 5.7. "Sens" button /see Instructions Manual/.
Set the titration speed to 3 by turning the 2.3. selector to position 3 /see the Instructions Manual/.
Set the comparison level to 9 by turning the 5.2. "Channel" selector to position 9 /see the Instructions Manual/.
Attach the cell to the titration head and titrate the solution with 2 M HCl.
Calculate the caustic soda by the calibration equation and the burette reading /see Instructions Manual/.

When the titration of caustic soda is over, add 15 cm^3 of KF to the titrated sample in the cell.
Turn the 2.11. and 2.12. taps into "suction" /◷/ position to refill the cylinders and reset the display /see Instructions Manual/, then titrate the solution with 2 M HCl.
Calculate the alumina by its calibration equation and the burette reading /see Instructions Manual/.

Note: Sodium carbonate can also be determined in this solution. See the Instructions Manual, Analytical Methods, for details. This procedure is omitted from the laboratory experiments.

4. DETERMINATION OF MAIN COMPONENTS OF RED MUD BY ATOMIC ABSORPTION SPECTROMETRY /AAS/

PRINCIPLES

Scope of AAS

In the last twenty years atomic absorption spectroscopy /AAS/ has become the most widely used analytical procedure for the determination of the metallic elements. This method has come into general use in the alumina industry due to its relatively low expenses and simple sample preparation techniques. The detection limit of AAS is low, especially by using electrothermic atomization /ETA/, therefore, it can be used for trace metal analysis. On the other hand, flame AAS can also be applied for the determination of major metallic constituents with a high precision. A typical relative standard deviation /RSD/ of 1 - 0.5 % can easily be achieved by a conventional flame AAS instruments. Using a nitrous-oxide - acetylene flame one can analyse the refractory metals, which are very important in the alumina industry, because almost every sample contains Al, Si, Ti, etc. refractory elements.

AAS can control technology through the analysis of the main components of red mud or bauxite, and products of different digestion experiments, due to its good reproducibility, little time- and sample consumption as well as operation economy. To improve productivity a complete analytical system is organized.

Description of the method

Sample dissolved in an appropriate solvent is sprayed into a flame or evaporated electrothermally. The atomized vapor is irradiated by resonant light from a special spectral lamp. The wavelength of the absorbed light is characteristic of the element concerned and the absorption is proportional to its concentration in the vapour.

The resonant light source provides the spectral lines of a single element, thus AAS is a single-element method. Due to the small number of resonant lines, spectral interference has rarely to be considered.

Atomization efficiency depends on a number of different factors such as the viscosity and surface activity of the solution, quality of the component and the matrix to be analysed, design of the atomizer, the uptake rate of the sprayer, the temperature depending on the chemical composition of the flame and the character of the gas flow /i.e. construction and shape of the burner head/. The quality of the flame atomizing system is decisively important concerning the accuracy of the analytical result.

The AAS method is a relative method, thus the light absorption of suitable reference solutions is compared with that of the sample. Because of the high precision required concerning the main components the standards have to be prepared very carefully, preferably with concentrations that bracket the unknown samples.

EXPERIMENTAL

The AAS instrument consists of an atomizer, the resonant radiation source, light dispersion system and a light intensity meter.

The task of the nebulizer and atomizer unit is to produce atomic vapour in which the concentration of the component concerned is proportional to the concentration of the component in the original sample. Sprayers, gas burners electrically heated graphite tubes or metal ribbons are used for this purpose. The AAS equipment is generally supplied with a flame atomizer. The heated graphite tube has become the most popular amongst different ETAs. ETA system as the most sensitive analytical technique is generally used for trace analysis of metals. Its further advantage is that small amount of sample is required.

Hollow-cathode lamps are generally used in AAS as light sources. For certain elements higher sensitivity can be achieved when applying electrodeless discharge lamps /EDL/. With the modern instruments using modulation of the heating current, life time of about 2000 hours can be achieved. In AA spectrometers normally 3-6 lampholders are provided.

A single or in the more sophisticated instruments a double-beam optical system serves as a light dispersing unit. Corresponding to the ultraviolet and visible range of wavelength, furthermore, the thermal stress optical system is used which is made of quartz or quartz-lined units having a medium resolution power /dispersion of 3-6 nm/mm/. A deuterium lamp is normally installed for the correction of the background radiation.

Light intensity is measured by a photomultiplier. Modern devices contain a microprocessor which provides digital display of absorption, enable auto-zero setting and measurement under various integration times. Direct display of concentration and curve correction facility is often provided. The AAS instrument can also be used in emission mode /as flame photometer/.

Enabling the analyses of large number of samples automatic sample changers are expediently used.

The automation of AAS is highly developed, modern AAS instruments include microprocessors. Due to the microprocessors, modern instrumentation is versatile and relatively easy to use.

Complex analytical system based on AAS

The parts of the complex AAS analytical system developed in ALUTERV-FKI are as follows:

a home made sequential fusion apparatus,
Pye-Unicam sample changer /SP450/,
Pye-Unicam AAS instrument /SP 1900/,
Solatron data transfer unit,
Facit tape puncher,
Hewlett-Packard desk calculator /9830/.

The flow-chart of this system is shown in Fig.2.

The solutions of red mud /or bauxite/ samples made by fusion of sample with strontium carbonate - boric acid

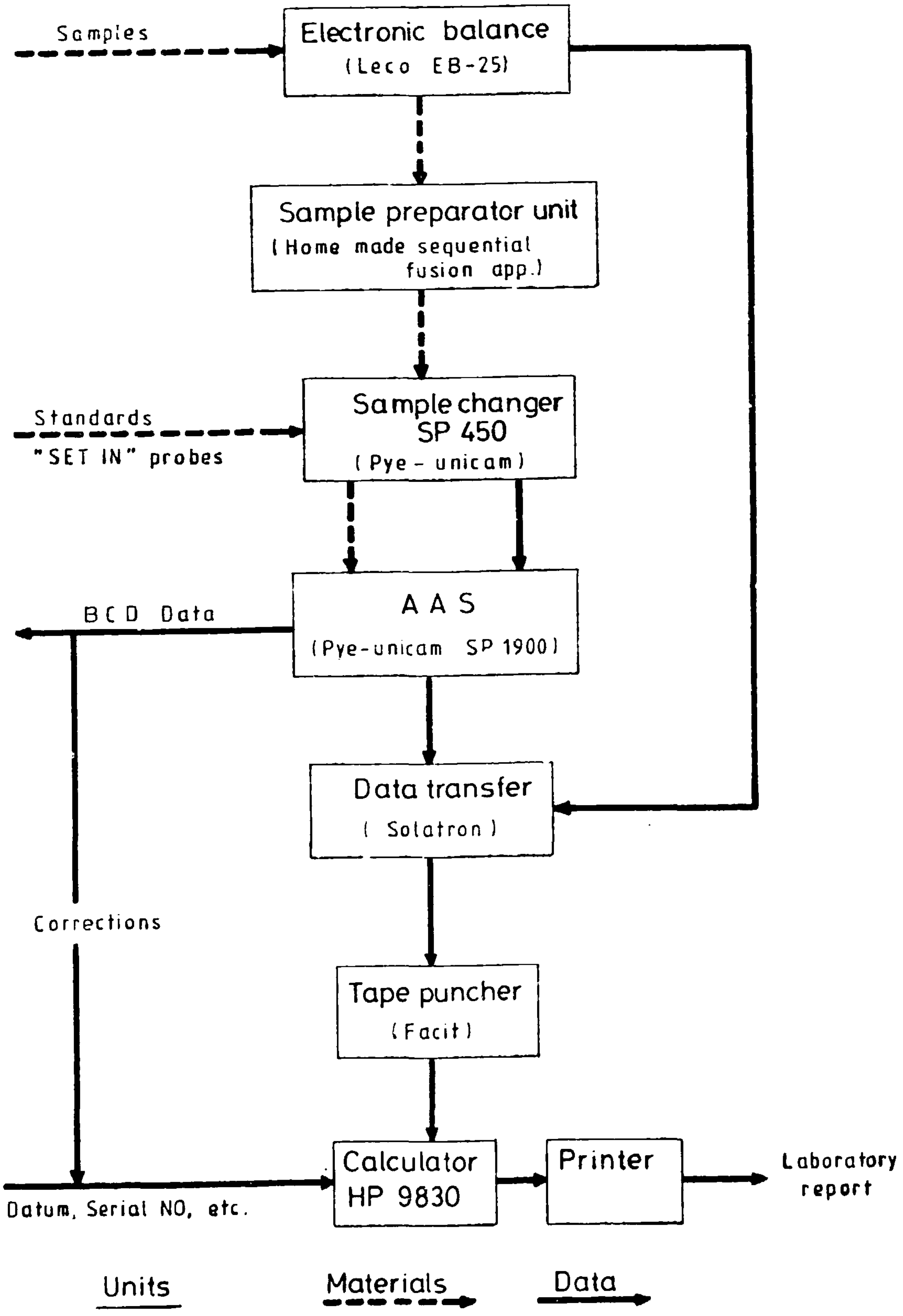

Fig.2. Flow chart of the AAS analytical system

flux and dissolved in diluted hydrochloric acid are taken to the sample changer. The AAS instrument works with parameters selected according to the components to be determined. The intensity data are recorded on a punch tape and entered into the calculator. The result is printed as a laboratory report.

Sodium concentration of red mud and bauxite samples is measured by the same AA spectrometer in flame photometer mode.

Results are calculated from the intensity data by a Texas SR 52 programmable pocket calculator.

PROCEDURES

Sample preparation

Weigh in eight different air-dry red mud samples /0,2 g of each/ to platinum crucibles and 2 g of flux /1:1 mixture of strontium carbonate and boric acid/. Take the crucibles to the sequential fusion apparatus after ignition of both flames. Set the temperature of both flames by adjusting the ratio of gas and oxygen. Select fusion time with the two push buttons 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 until fusion is finished. 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 /some hours waiting/

and transfer the solution to a 200 ml volumetric flask washing the beaker and crucible with distilled water and fill up to the mark.

Sodium analysis

Weigh in 0.5 g of air-dry red mud samples as well as one standard red mud sample 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. Boil the mixture 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 5 ml/ to a 100 ml volumetric flask after sedimentation. Fill up to the mark with double distilled water and measure the sodium concentration in flame photometer mode.

Installation of AAS

Place clear cups onto the tray of the sample changer and pour the sample solutions, "set in" probe solution and standard solutions as well as distilled water to the fifty cups according to the given order. The standard solutions consist of required quantity of flux, hydrochloric acid and different volumes of the Al, Fe, Ti, Si, Ca, and Mg standard solutions 1 to 5 in growing order.

The third standard solution can be used as "set in" probe. For checking of the operation of AAS analytical system one of the standard red mud solutions of known composition is applied on each tray.

Having become familiar with the construction and operation of the AAS, switch on the main instrument /SP 1900/, the sample changer, data transfer unit and the tape puncher. The basic installation of these instruments can be studied in the instruction manual /supplied/.

Check the acetylene, compressed air and nitrous oxide gas supply and set gas control valves to the required position.

Caution!

Acetylene - air and acetylene - nitrous oxide mixtures can be dangerously explosive. Never leave the instrument unattended with the flame burning. A proper exhaust system must 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 /see tables/, set the suitable lamp current and find the element line by turning the monochromator control to the required wavelength. Ignite and adjust the flame according to the element. /For Al, Si, Ti analysis acetylene - nitrous oxide flame is to 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.

For the sodium determination adjust the wavelength for the sodium D line, 589 nm. Set the sensitivity or scale expansion control to give the reading 600 on the display for the 100 ppm standard solution aspirated. For zeroing use double destilled water.

Al, Si, Ti, Ca, Fe and Mg determination by AAS

/i/ Set the sample changer to tray position 1,
/ii/ put the aspirator capillary onto the sampling arm,
/iii/ select the 4 sec integration interval,
/iv/ start the sample changer in double mode,
/v/ start data transfer and tape puncher,
/vi/ wait until all the fifty samples are aspirated,
Note: The operation of the instrument can be controlled by watching the values on the display.
/vii/ change the lamp for the next element in the sequence Al, Si, Ti,
/viii/ select the required sensitivity range,
/ix/ repeat the previous procedures /i/ to /vi/,
/x/ change gas from nitrous oxide to air,
/xi/ repeat procedures /i/ to /vi/ for Ca, Fe and Mg.

Sodium determination

/i/ Install the instrument in flame photometer mode,
/ii/ select integration period of 4 sec,

/iii/ measure the sodium intensity aspirating all the sample solutions.
Note: Check the intensity of the standard solution after every fifth sample.

Calculation of the concentrations from intensity data

Sodium

A Texas SR 52 programmable pocket calculator is used for the evaluation of sodium content of the samples. The moisture corrected equation and the calibration curve from 2.5 ppm to 15 ppm sodium solution are recorded on a magnetic card. Load in the program, type in the weights, moistures and intensities of the red mud samples using the data file keys on the calculator and read the sodium content off the calculator display in percent units.

Other elements

Collect the weight, loss on ignition and sodium content data from other experiments. Take the punch tape with the recorded intensity data on it to the computer HP 9830. Calculate the result according to the user and program manual.
Note: The flow chart of the program can be seen in Fig.3. The results are printed on the selected printer.

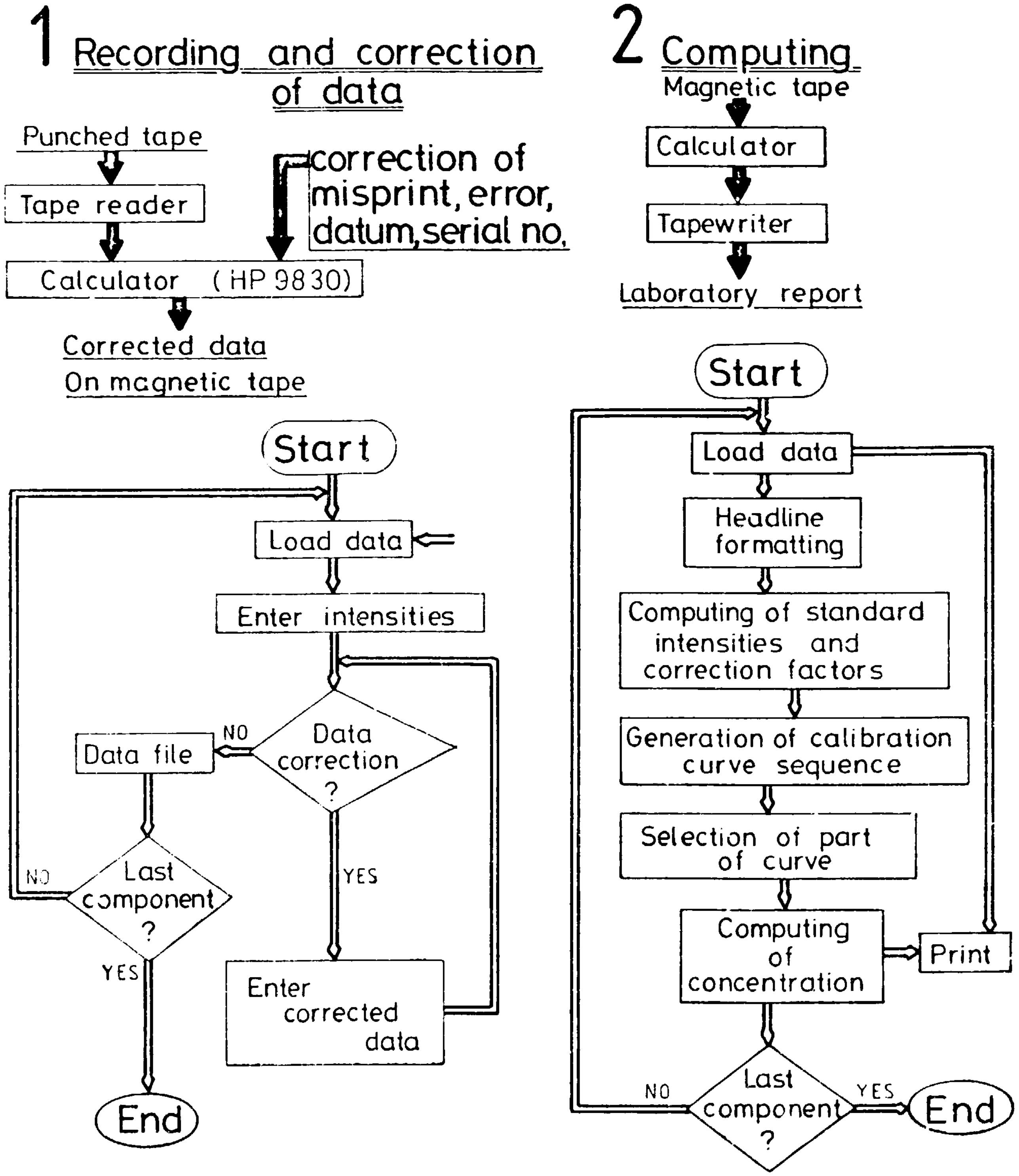

Fig.5. Flow chart of a computerized data processing system

5. CHEMICAL ANALYSIS OF ALUMINA

Alumina produced by the Bayer-technology contains at least 98 % of Al_2O_3. The properties of aluminium made of alumina strongly depend on the impurities. The impurities which are the most important from the aspect of the aluminium metallurgy, SiO_2, Fe_2O_3, TiO_2, V_2O_5, P_2O_5, Cr_2O_3, CuO, ZnO, MnO_2, CaO and total Na_2O can simultaneously be determined by optical emission spectroscopy /OES/, without the need for dissolving the sample. Determination of the sulfur and carbon content of alumina is based on a different principle, namely the infrared absorption of the CO, CO_2 and SO_2 gases produced by burning the sample in oxygen atmosphere in an induction furnace. During the practice, we shall focus our attention to the former method, the OES.

PRINCIPLES

Origin of atomic spectra

OES is based on the phenomenon, that electrons having been excited from a so-called valence state to a higher energy state through thermal or electric excitation, jump back to their ground /or lower energy/ state by releasing a photon of the corresponding frequency, ν:

$$E = h\nu$$

where E is the energy difference between the two states, h is the Plank´s constant. The lifetime of such an excited state is of the order of 10^{-8} sec. Since the various elements have different energy level patterns, the frequency /or the wavelength/ of the emitted photons is characteristic of the element and the number of the emitted photons depends on the concentration of the elements concerned.

Optical emission spectroscopy /OES/

OES consists of the following processes:

atomization and excitation of the sample in the high temperature plasma /e.g.d.c. arc plasma, spark plasma, inductively coupled plasma, etc./,

resolution of the emitted light by optical prisms or gratings,

measurement of light intensity using photographic plates /spectrograph/ or photoelectron multipliers /spectrometers/.

The emission spectrum of the plasma consists of spectral lines of atoms and ions, bands of molecules and a continuous background radiation. Wavelengths between 180 nm and 800 nm are of particular importance for the purposes of chemical analysis.

Relationship between line intensity and concentration

The relationship between the concentration c of the element in the plasma and the intensity I of its spectral line is given by the Malcipa equation:

$$I = Ac^{n}$$

where A and n are suitably chosen constants.

The relationship holds for all spectral lines of the element which are free from self absorption - provided that the experimental conditions remain unchanged. The effects of the sometimes irreproducible experimental conditions may be eliminated by the application of a reference element which, in most cases, is the host material. The line intensity of the element concerned and that of the reference material - is effected in the same way, therefore we formulate the Malcipa equation for the relative quantities:

$$C' = \frac{C_x}{C_r} = a \left(\frac{I_x}{I_r}\right)^{\eta}$$

where C_x and C_r are the concentrations, I_x and I_r are the line intensities of the element to be analysed and the reference material, respectively, a and η are constants which can be determined experimentally.

The logarithmic form of the equation is an easy-to-handle linear relationship:

$$\lg C' = \lg a + \eta \lg \frac{I_x}{I_r} = \lg a + \eta \Delta Y_{x,r}$$

Accordingly, the linear relationship between the logarithm of the concentration and that of the intensities of the analytical line pair yields an analytical curve the slope of which is equal to $1/\eta$ /See Fig. 4./.

In possession of the "blackening curve" measured densities /keeping exposure time constant/ can be converted into lg I = Y values. Table 6. lists the emission line pairs of elements of importance in the OES of alumina.

Table 6.

Element	Line pairs	Concentration range
Si	Si 288.6 /Al 306.43	0.003 - 0.1
Fe	Fe 275.57/Al 306.43	0.003 - 0.1
V	V 318.4 /Al 306.43	0.001 - 0.5
Ti	Ti 334.9 /Al 306.43	0.001 - 0.1

Photographic measurement of the light intensity

Light is detected in OES using light sensitive photographic plates. On irradiation, a reduction of silver takes place in the emulsion and the plate blackens. We normally observe the developed photographic plates by means of transmitted light, therefore, the optical density of the plate is defined as:

$$S = \lg /i_0/i/$$

where i_o and i are the incident and transmitted light intensities, respectively /in a photometer/.

When a photographic emulsion is activated by radiation, the density, S, is a function of the wavelength, the intensity of the radiation, I, and the exposure time, t. This function may be written as

$$S = k . I . t^p$$

where k and p are constants, the latter is a function of the wavelength.

Fig. 5. shows the above relationship in its logarithmic form. The middle, linear region of the curve is preferably used for analysis, but, for trace analysis, measured densities have to be corrected according to the characteristic curve of the emulsion to get intensities which relate to the concentration of the element through the Malcipa equation.

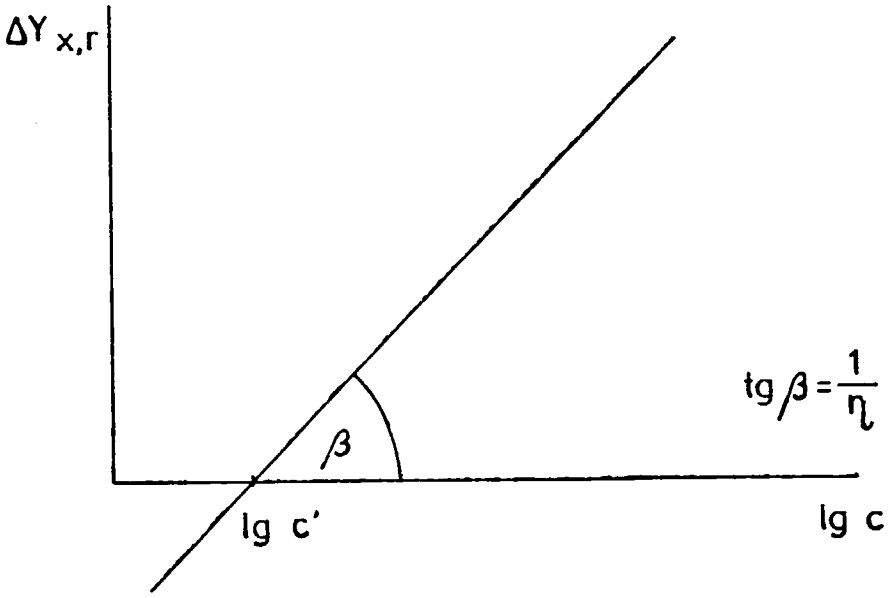

Fig.4. Scheme of an analytical relationship in OES

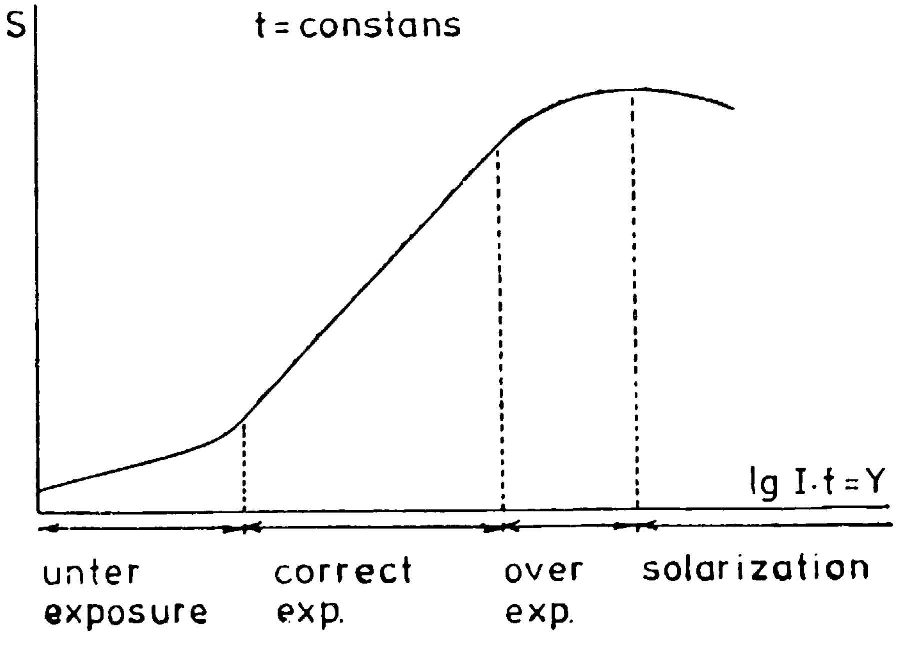

Fig.5. Blackening curve of the photographic emulsion

EXPERIMENTAL

Apparatus

Q 24 quartz spectrograph with photographic system, d.c. power supply, stopwatch, phototechnical apparatus, spectrum projector, microdensitometer, calculator.

Materials

Graphite cup and needle electrodes, graphite powder, standard series of alumina samples, corundum mortar, Agfa Gevaert 34-B-50 photographic plate.

PROCEDURE

OES analysis consists of the following tasks: preparation of the sample, taking spectrograms, development, observation and evaluation of the plates.

Mix standard alumina samples in a corundum mortar with high-purity graphite in a ratio of 1:2 and fill up the graphite cup electrodes /three per sample and per standard/ with the so obtained mixture.

Fix a filled cup electrode and a graphite needle counterelectrode into the electrode stand 2 mms apart, adjust the electrode gap in the optical axis of the spectrograph.

Adjust a 15 /um slit onto the slit-head of the spectrograph and onto the filter.

Connect the electrodes to the d.c. supply, applying the cup electrodes as the anode.

With the discharge switch "OFF", switch on the d.c. supply and set the current to 6 Amps.

Place the photographic plate into the spectrograph cassette.

Switch on the exhauster.

Withdraw the cover plate of the cassette, remove the slit cover.

Switch on the lamp illuminating the wavelength scale for 5 seconds and move the cassette on.

Initiate a discharge by the discharge switch, let the sample evaporate completely, measure the evaporation time by the stopwatch.

When the spectrogram is ready, switch off the current, replace the slit cover and move the plate holder on.

Before starting the next exposure, change and adjust the electrodes, remove the slit cap.

Make every new spectrograms in the same way.

As the last exposure, take up a Fe spectrum with an a.c. arc between two iron electrodes. This will facilitate the use of the spectrum chart.

Put the cover plate of the cassette back.

Development of the photographic plates

Use an AGFA 1 developing bath at 20 deg. C temperature. Immerse the plates for 4 minutes, rinse them in water, then fix them for 15 minutes. Rinse again in water for 30 minutes and dry the plates.

Densitometry of the plates

Determine the intensities of the analytical line pairs /see Table 6./ from the plate densities measured by the Zeiss G-II type microdensitometer /attached to a TEXAS 59 calculator according to the user´s manual.

On the basis of the calculated $\Delta Y_{x,r}$ values measured in the standard series, plot the analytical curves.

In possession of the $\Delta Y_{x,r}$ values of the unknown sample, read the unknown concentration off the analytical curves.

6. X-RAY DIFFRACTOMETRY

PRINCIPLES

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

a./ The powder pattern of a substance is characteristic of it, and can be used for identification much as fingerprints are used for the identification of human beings.
Peak positions corresponding to directions /diffraction angles 2θ/ in which a positive interference of X-rays occurs, fulfil the Bragg-condition:

$$\lambda = 2d.\sin\theta \qquad /1/$$

where λ is the wavelength of X-rays, d is the spacing of particular atomic planes. Relative intensities of diffraction lines in a powder pattern of a substance are determined by the "strength" of the local oscillator, namely the atoms in the crystal lattice.

b./ Absolute intensity I_{ij} of the j-th line of substance i in the pattern of a multicomponent powder mixture relates to the weight fraction x_i /i = 1, 2, ..., n, the number phases in the mixture/ by the formula:

$$I_{ij} = \frac{K_{ij} . x_i \; R_{ij}}{\rho_i \; \mu_T} \qquad /2/$$

where:

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

ρ_i - is the density of phase i,

μ_T - the total mass absorption coefficient of the specimen including phase i, i.e $\mu_T = \sum_{1}^{n} x_j \mu_j$
Since μ_T depends on x_i, I_{ij} is not strictly proportional to x_i. The deviation is usually called the matrix effect,

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

Relationship /2/ between molar fraction x_i and intensity I_{ij} can not be established unless the sample consists of an enormous number of very tiny crystals of 100 μm in size, or smaller, with completely random orientation.
Penny-or needle-like crystallites, however, tend to prefer certain orientations. Preferred orientation in certain crystallographic directions may drasticly effect measured intensities and, by any means, is to be avoided, if possible.

Methods of X-ray diffractometric phase analysis

Qualitative analysis of a powder pattern /either film or diffractogram/ starts with the measurement of peak positions and intensities, and proceeds with the calculation of interplanar spacings, using eq /1/. Then a comparision of the data with some systematic file of standard patterns follows. Different types of search for matches between known and unknown patterns are used /Hanawalt, Fink, etc./ but a filter of data by any knowledge of chemical composition of the sample is of great importance.

The various methods of quantitative XRD use different forms of eq /2/.

Absolute intensity method

When only one component is sought and its measured intensity is referred to a scale corresponding to pure component i, eq. /2/ has the following form:

$$I_{ij}/1/x_i=1/ = /u_i//u_T \cdot x_i \qquad /3/$$

where only μ_T is unknown.

Depending on the difference between the mass absorption coefficient of the phase i and the rest of the sample, calibration curves may deviate from a straight line either upwards or downwards.

This method needs numerous, complex and variable calibration for multicomponent systems. However, it is a fast method for phase analysis of samples with phases of very similar mass absorption coefficients. /E.g. mass absorption coefficient of different aluminas is very close to each other, thus the calibration curve for any of them is a straight line/.

Internal standard method

Dependence of I_{ij} upon the absorption can be eliminated from eq /2/ relating I_{ij} to the t-th line intensity of the phase s:

$$I_{ij}/I_{st} = \frac{K_{ij}\cdot R_{ij}\varrho_s\cdot x_i}{K_{st}\cdot R_{st}\varrho_i\cdot x_s} = \text{const.}\cdot\frac{x_i}{x_s} \qquad /4/$$

Now component s can be considered as an internal standard to which component i is referred. Since K_{ij} contains apparativ parameters as multiplying factors $K_{ij}/K_{st}=k_i/k_s$, where k_s depend only on the phases i and s if we restrict ourselves to the strongest lines. The k factors are aften called intensity conversion factors /ICF-s/. Knowing I_{ij}/I_{st} versus x_i/x_s, one only needs to mix the sample with known amount of the standard material and to measure the intensity ratios. Weight fraction of phase i can be read off the calibration curve. Since the absorption coefficient has been eliminated, eq. /4/ always represents a straight calibration curve which can be characterised by its slope k_i/k_s.

Dilution with unknown method

It is sometimes easier to dilute the specimen with known amounts of the component, the concentration of which is to be determined. In this case neither the amount nor the identity of the standard component s need to be known / dilution with unknown method /. The intercept of the line fitted to the intensity /in units of any line intensity of phase s/ versus added-unknown-points with the axis of added unknown gives the fraction of the unknown component in the original sample. /Fig. 6/.

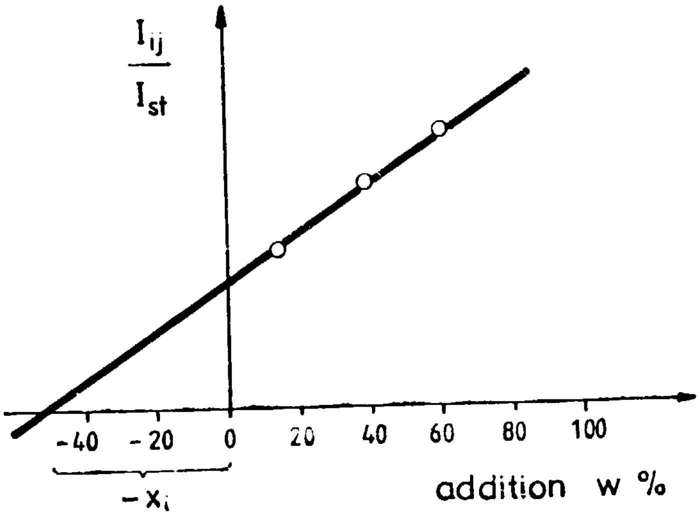

Fig.6. Dilution with unknown method. The straight line fitted to the intensity vs addition points intercepts the abscissa at - x_i.

Quantitative XRD without standards

In the case of n identified components in the specimen, one has n equations of type /2/, but only /n-1/ measured intensity ratios consequently /n-1/ equations of type /4/. If and only if the qualitative analysis is complete, one has a normalisation condition for molar fractions x_j: $\sum_{j=1}^{n} x_j = 1$ which can be used as the n-th equation. The solution of the linear equation system has a symmetrical form:

$$x_i = \left(\frac{k_i}{I_i} \sum_{j=1}^{n} \frac{I_j}{k_j} \right)^{-1} \qquad /5/$$

Methods introducing chemical information

All the methods mentioned above require the knowledge of the calibration curves or ICF-s, or at least material available of the pure unknown component with the same ICF as in the sample. In the case of minerals, like in bauxites, a very wide spread of ICF-s has been found, depending on the geohistory of the ore. The same applies for materials from different technological processes. The best one can do is to minimize the effect of ICF-s on the phase analysis. A computer version of this algorithm for bauxites is presented in detail in the theoretical lectures /Vol.4., Chapter 2/. ICF-s and composition of bauxite are listed in Tables 7 and 8., respectively.

The aims of this practice are the following:

a./ introduction to the different experimental methods and problems of XRD /sample preparation, choosing the right experimental conditions for the diffractometer, etc./,

b./ qualitative and quantitative evaluation of diffractograms of artificial mixtures,

c./ checking calcination performance by quantitative determination of corundum content of alumina samples,

d./ checking dissolution efficiency by qualitative analysis of red muds,

e./ application of a complex method for bauxite phase analysis.

Table 8. Intensity coversion factors, their standard deviation and the relative intensity conversion factors

Phase	ICF*	STD	RICF
Hematite	2.6	1	1
Boehmite	1	0.1	1
Cancrinite	5	2	5
Sodalite	6	2	6
Perowskite	0.2	0.1	0.3
Goethite	2.7	0.9	1.2
Corundum	0.42	0.05	0.42
Gibbsite	0.9	0.2	1.2
Diaspore	1	0.2	1
Kaolinite	5.4	1.5	5.4
Ca-aluminate	2	1	3
Na-titanate	5	2	12
Ilmenite	1	1	1
Siderite	0.3	0.1	0.6
Magnetite	0.3	0.1	0.1
Lithiophorite	4.9	1	4.9
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
Crandallite	5	2	2

* Relative to boehmite

Table 7. Chemical composition of some bauxite phases

	Al_2O_3 %	Fe_2O_3 %	SiO_2 %	TiO_2 %	CaO %	MgO %	FeO %	P_2O_5 %	Mn_3O_4 %	CO_2 %	S %	L.O.I. %
Boehmite	85.0											15.0
Gibbsite	65.4											34.6
^{x}Diaspore	85.0											15.0
^{x}Hematite		100.0										
^{x}Goethite		89.9										10.1
Magnetite		103.5					31.1					-3.5
^{x}Siderite		68.9								38.0		31.1
Pyrite		66.7					59.8				53.5	-33.3
Ilmenite		52.6		52.7			47.3					
Anatase				100.0								
Rutile				100.0								
^{x}Calcite					56.0					44.0		44.0
Dolomite					30.4	21.7				47.9		47.9
Quartz			100.0									
Crandallite	37.0				13.5			34.3				15.2
Lithiophorite	25.3								56.8			17.9

x Phases of variable composition /to be determined from line shifts/.

EXPERIMENTAL

Sample preparation

Specimens are made from previously ground materials /particle size less than 63 /um/ by pressing the powder into a thin aluminium sample holder /Fig. 7/. Put a piece of abrasive paper on the press tool and fit the sample holder onto the metal peg. Pour the powder on the rough surface of the abrasive paper and smooth it with the spatula. Put the counterpart on the top of it, slip the whole tool into the press and tighten it. Undo the press and the tool and cover the back of the sample with a flexible cover-plate. Gently slip the sample holder into the magazine until it hits the back of the magazine /Fig. 8/. Make a note of the sample position and identity.

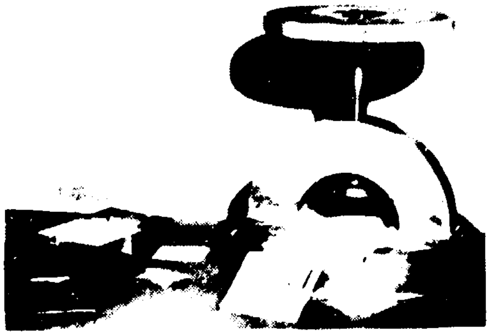

Fig.7. Hand press for preparation of powder samples

Description of the diffractometer

The block diagram of a conventional XR diffractometer can be found in the Chapter 2. of vol. 4 /see figure 4.14/. XRD equipment to be used for group training is based on commercial Philips units, but it has been modified to make serial measurements more comfortable. A fast return motor has been mounted on the goniometer /Fig. 9./, the chart motion and low angle start of the goniometer has been synchronised such a way that the angle position markers coincide with the thick lines on the chart to help reading peak positions. Additionally, a sample selector unit is connected to the automatic Philips sample changer. Two scalers are used in a flip-flop mode to avoid wasting counts during printing time. The printer is replaced by a paper tape puncher to record diffractograms for off line evaluation by a computer.

PROCEDURE

Switch on the 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. Make sure that the cooling water of the generator and the X-ray tube is on. Wait 15 second then turn the high voltage on by pressing the two adjacent H.V. buttons simultaneously, than releasing the one marked "0". Turn the HV up to 45 kV, then the tube current up to 40 mA. Insert the filled magazine into the sample changer and fit the gears appropriate for the chosen goniometer speed /see the possible combinations on the goniometer/. Set the angular limits by loosing and tightening the bolts L - low angle limit and H - high angle limit /see Fig. 9/.

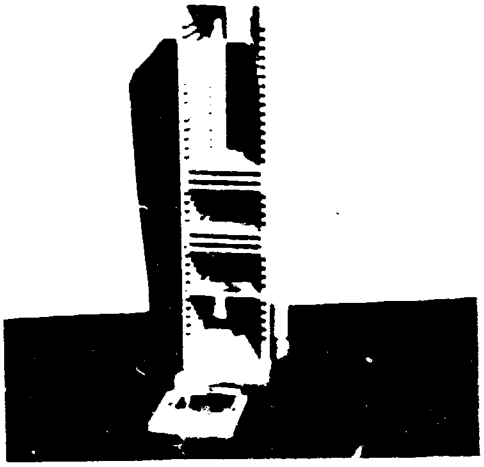

Fig.8. Sample magazine

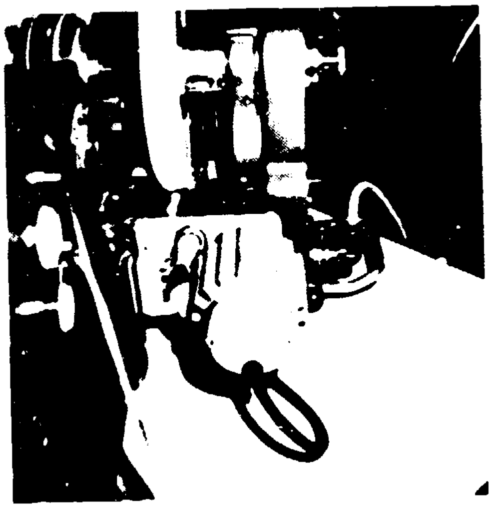

Fig.9. Modified Philips goniometer with fast return motor /RM/. L - Low angle limit, H - high angle limit

Set the time constant of the ratemeter to the highest value, which satisfies the condition:

$$s \cdot \tau \leq 4 \qquad /6/$$

where s is the goniometer speed /degree per minute/, τ is the time constant in seconds. This condition guarantees that peaks will not be overintegrated. Set "sample selector" switch to the position of the sample in the magazine to be recorded first and press button "Ready". Recording may be started by pushing "START" on the front panel of the "sample changer control". Then open the X-ray shutter 2 by pushing the buttons "2" and "Shutter" in the same time. Now the diffractometer is ready for operation.

Caution!

X-rays are harmful to the human body, especially to the eyes. Please, do not touch the radiation shielding between the X-ray tube and the detector. In normal use the equipment is radiationproof. When high voltage is off, no X-rays are generated.

Quantitative determination of the α-alumina /corundum/ content of an alumina sample by the absolute intensity method

Prepare four parallel samples from the material and use the 100 % alpha-corundum standard /available in the laboratory/

as a reference, to 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. Use sensitivity: 2×10^3 cps. Find the diffraction peak of corundum at $2\theta=25.6^{\circ}$. Set the lower angle limit slightly below 24° and mount the gears which are appropriate for 0.5°/min. goniometer speed. Switch on the printer and turn the preset count switch to ∞ /on the scaler/. .Preset measurement time to 100 secs on the timer PW 4261. When the sample moves in, start the scaler. When the scaler stops, reset it and preset measurement time to 200 secs. After this measurement count background for 100 secs again. When the next sample moves in, repeat the whole procedure. The printer reads out the scaler when the scaler stops. Determine peak intensity by subtracting the sum of the two intensities measured for 100 secs from the one measured for 200 secs. /See Fig. 10. for explanation/. Calculate the concentration of α-alumina by relating the measured peak intensities of corundum in the unknown and in the standard samples respectively:

Calculate mean and standard deviations for the four parallel samples.

Quantitative determination of hematite in an unknown ternary mixture by the dilution 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 percent of hematite are supplied.

Study the diffractogram of the unknown /chart available/. Mark and identify the peaks of hematite. Identify the rest of the lines /two phases/. Tables are available in the laboratory. Select the shortest 2θ interval in which all the three phases have at least one single, nonoverlapping peak with high enough /> 30 percent/ relative intensity. Set the angle limits and take a 0.5°/min. record of the three samples /"U", "U+20", "U+40"/ within the chosen angle interval.

Determine the integrated intensities of the peaks supposing a linear background and estimating the area of the peaks by that of a triangle /see Fig. 11/. Proceed as described in the paragraph "Dilution with unknown method". Determine hematite content in Sample "U" from the intercept on a graph similar to Fig. 6 .

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 /relative to corundum/ from the JCPDS Index and use the formula /5/.

Qualitative analysis of a red mud diffractogram

Mark and identify the peaks on the chart and make a note of the phases present in the sample. Pay attention to the aluminium phases left in the mud and silicates beside the

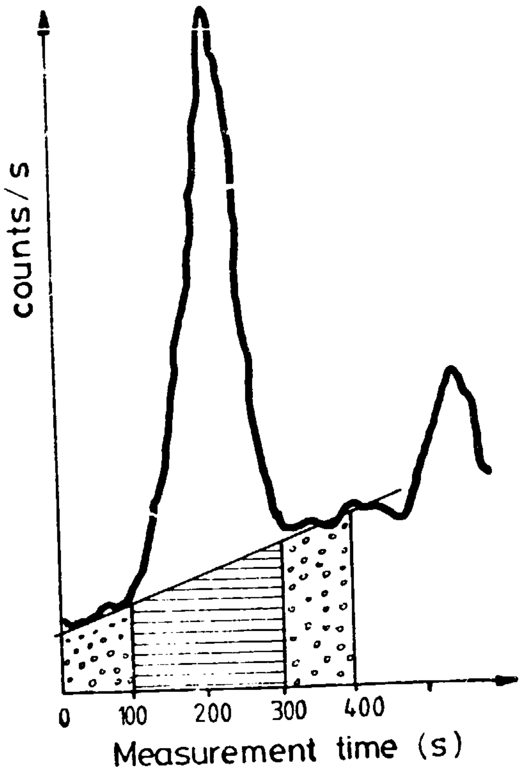

Fig.10. Background correction. The area of the two dotted regions is equal to that of the striped one

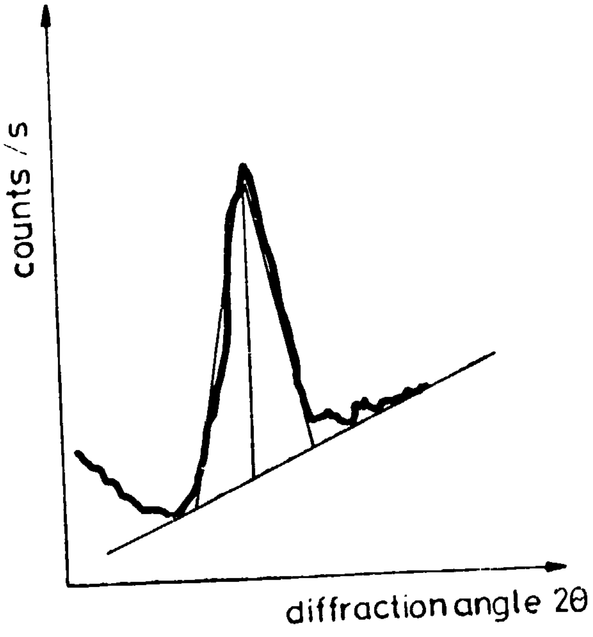

Fig.11. Approximation of peak intensity by the triangle method

main red mud phases. Make use of the knowledge of the technology and data of the chemical analysis /available/.

Quantitative phase analysis of a bauxite sample by the complex method described in chapter 2. of the vol. 4.

/i/ by "hand evaluation" of the record

/ii/ with the aid of the HP 9830A desk-top calculator /demonstration/

Procedure for hand evaluation:

/i/ Complete qualitative analysis of the diffractogram using determinative tables.

/ii/ Determine foreign atom substitution in goethite, hematite, diaspore, calcite or siderite /if there is any/ from line shifts. Correct the compositions according to the calibration curves /line shifts versus mole per cent of substituted foreign atoms/ available in the laboratory.

/iii/ Determine the integrated intensities of the lines on the chart by the triangle method make corrections for overlapping peak intensities.

/iv/ Allocate oxides to phases according to the chemical composition of phases /Table 7. / making use of formule /5/. The relative intensity conversion factors and their standard deviation are given in the Table 8.

/v/ Recalculate the phase composition with modified relative intensity conversion factors /but within the interval marked in Table 7./ starting from the point d./ if either the L.O.I., or the sum of the phase percentages significantly deviates from the values analysed chemically.

Take part on the demonstration of computer version of the phase analitical method described above.

7. THERMAL METHODS OF ANALYSIS

PRINCIPLES

All the physical and chemical phenomena, like phase transformations, chemical reactions, crystallization and others are accompanied by changes in certain physical parameters of the matter, like mass, volume, internal energy, electrical resistance, etc. The phenomena and the matter can sensitively be studied by analysing changes in these parameters.

Thermal methods of analysis include techniques in which some physical parameter of the system is measured as a function of temperature, methods like thermogravimetry /TG/, differential thermogravimetry /DTG/ and thermal analysis /DTA/, thermodilatometry, thermoluminescence, calorimetry, thermometric titrimetry, and others. In the following, we shall restrict ourselves to TG, DTG and DT analyses.

Differential thermal analysis /DTA/ is a technique in which the heat effects, associated with transformations in the specimen, are recorded as a function of temperature or time as the substance is heated at a uniform rate. Heat or enthalpic changes, either exothermic or endothermic, are caused by phase transitions - such as crystalline structure inversions, sublimation and vaporization, dehydration reactions, dissociation reactions or decomposition reactions, oxidation and reduction reactions, destruction of crystalline lattice structure, and other chemical reactions.Generally speaking, phase transitions, dehydration, reduction and some decomposition reactions produce endothermic, whereas crystallization, oxidation, and some decomposition reactions produce exothermic effects. In DTA, the sample temperature is continuously compared with the temperature of an inert material, the difference in temperature being recorded as a function of furnace temperature or time.

For illustration the DTA curve of a kaolinite sample is shown in Fig. 12/a. The endothermic peak at 560°C indicates the loss of crystalline water, resulting in the destruction of the crystal structure. The exothermic maximum at 920°C corresponds to the crystallization of amorphous Al_2O_3 into gamma-Al_2O_3.

<u>Thermogravimetry</u> is a technique whereby a sample is continuously weighed as it is heated at a constant rate. The resulting weight change vs. temperature curve so obtained gives information concerning the thermal stability and composition of the sample. To illustrate the principle, consider the weight - loss curve or thermogram of calcium oxalate hydrate, as given in Fig. 12/b. Part A of the curve corresponds to a stable state of the substance with no change in weight. Part B corresponds to a weight change caused by the evolution of one mole of water per mole of sample, as described by the following reaction equation:

$$Ca/COO/_2 . H_2O \rightleftharpoons Ca/COO/_2 + H_2O\uparrow$$

the next two weight changes C and D can be interpreted by the following equations:

$$Ca/COO/_2 \longrightarrow CaCO_3 + CO\uparrow$$

$$CaCO_3 \rightleftharpoons CaO + CO_2\uparrow$$

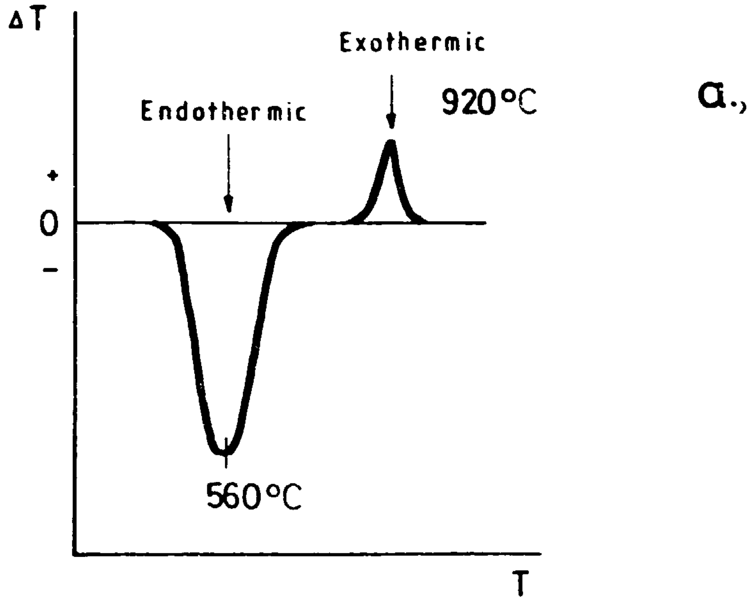

Fig. 12/a DTA curve of kaolinite

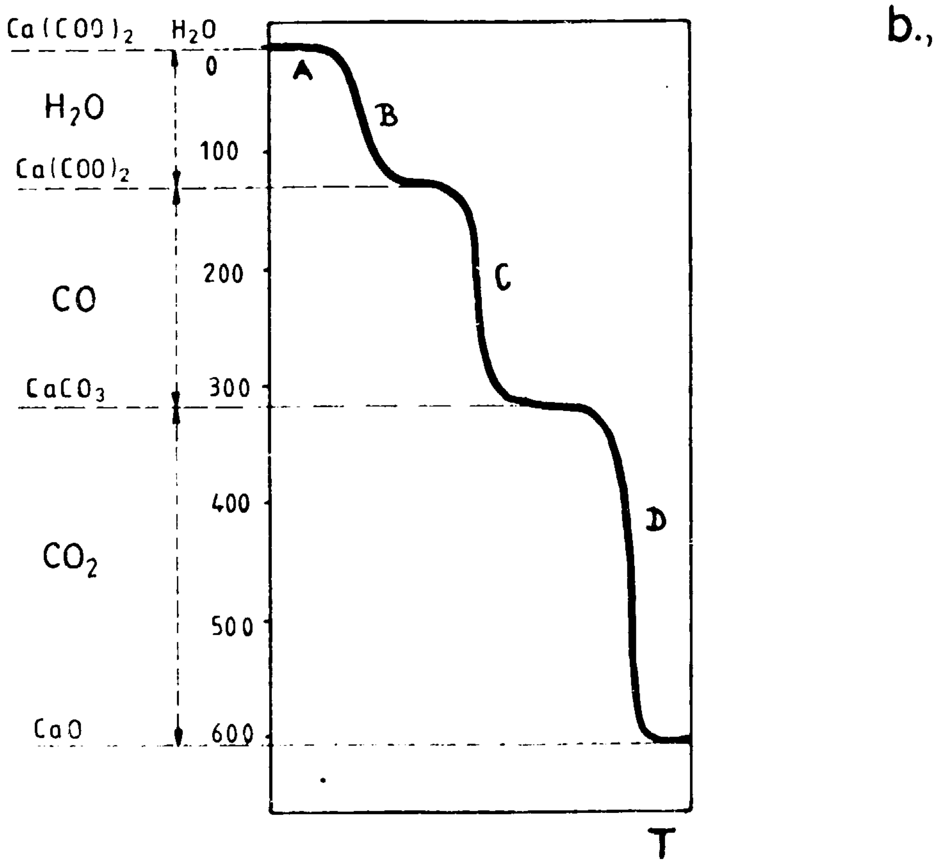

Fig. 12/b TG curve of $Ca/COO/_2 H_2O$

Thermogravimetry makes quantitative determination of the weight changes possible by measuring the step heights on the curve.

In differential thermogravimetry /DTG/, the rate of weight change, dw/dt, is recorded as a function of temperature or time. A series of peaks are now obtained, instead of the stepwise TG curve, with areas under the peaks proportional to the total weight change of the sample.

Differential thermograms can continuously be recorded using the principle of induction. A coil is attached to the beam of the thermobalance and suspended in homogeneous magnetic field. Sample weight changes cause a movement of the coil inducing a current, which is proportional to the velocity of the magnet, i.e. to the rate of change in weight.

The advantages and disadvantages of the three methods mentioned above can be summarized as follows:

DTA and DTG curves are comparable, however DTA indicates even those changes of state that are not accompanied by loss in weight. DTG curves are more reproducible.

Peaks on the DTA curves extend over a wider temperature interval, due to the subsequent warming /or cooling/ of the sample after reaction, depending upon the thermal conductivity and geometry of the sample. DTG indicates exactly the temperatures of the beginning, the maximum rate and the end of the change.

The area under the DTG curve gives the change in weight. /To avoid tedious planimetry, TG curves are usually recorded simultaneously/.

For the above reasons, DTA is primarily used for qualitative analysis, however DTG and TG can be used for quantitative analysis.

Qualitative and quantitative thermal analysis of bauxite

Decomposition temperatures of most of the frequently encountered bauxite phases fall into a reasonably temperature range, therefore DTA, DTG- and TG are important in the phase analysis of bauxites. In the majority of bauxites minerals decompose separately on heating i.e. interphase reactions do not take place. Knowing the volatile component of each mineral, one can calculate the phase composition from the loss in weight in a particular temperature range characteristic for the mineral /see Table 9./.

Complete mineralogical analysis /either qualitative or quantitative/ - can not be performed based solely on DTA and TG of bauxites, because certain phases /for example hematite, anatase, rutile/ are thermally inactive, some others have overlapping peaks. For example, gibbsite bleeds 2.5 moles of water up to 400 degrees C, the rest of water is lost at a higher temperature together with the decomposition of boehmite. Therefore it is to be subtracted from the weight loss of boehmite. On the other hand, boehmite contains more

Table 9. Transformations of frequently, encountered bauxite phases. Phases occurring most frequently in bauxites

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/18.02 Boehmite % = 119.96.G/18.02
Kaolinite $Al_2O_3.2SiO_2.2H_2O$		$2H_2O$	590-610	560-700	Al_2O_3 % = 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
Siderite	$FeCO_3$	CO_2	510-530	480-560	Fe_2O_3 % = 159.70.G/72 Siderite % = 231.70.G/72
Calcite	$CaCO_3$	CO_2	760-780	680-820	CaO % = 56.08.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

G - measured weight change in the given temperature range. For calculating boehmite the residual 0.25 mole water of gibbsite is to be subtracted than 1 mole of /about 1.33 moles/ water in bauxite samples. In phases of variable composition, /due to isomorphous substitution of some atoms by others in the crystal lattice/ the volatile content varies, too.

To overcome the above difficulties in thermal analysis of bauxites, complementary information /data of chemical analysis, X-ray diffraction, IR spectrometry/ is of particular importance.

Sample analysis of a boehmitic bauxite from Halimba area /Hungary/ is illustrated in Fig.13. and its evaluation based on complementary methods in Table 10.

EXPERIMENTAL

Derivatograph developed by L. Erdey, F. Paulik and J. Paulik and manufactured by the Hungarian Optical Works, combines TG, DTG and DTA measurements in one equipment.

Description of the derivatograph

The apparatus illustrated in Fig.14. consists of the following main parts:

- Furnace with sample and reference /Al_2O_3/ crucibles both with thermocouples for T and ΔT measurements, on a porcelain tube attached to the beam of the balance /through the bottom of the furnace/.

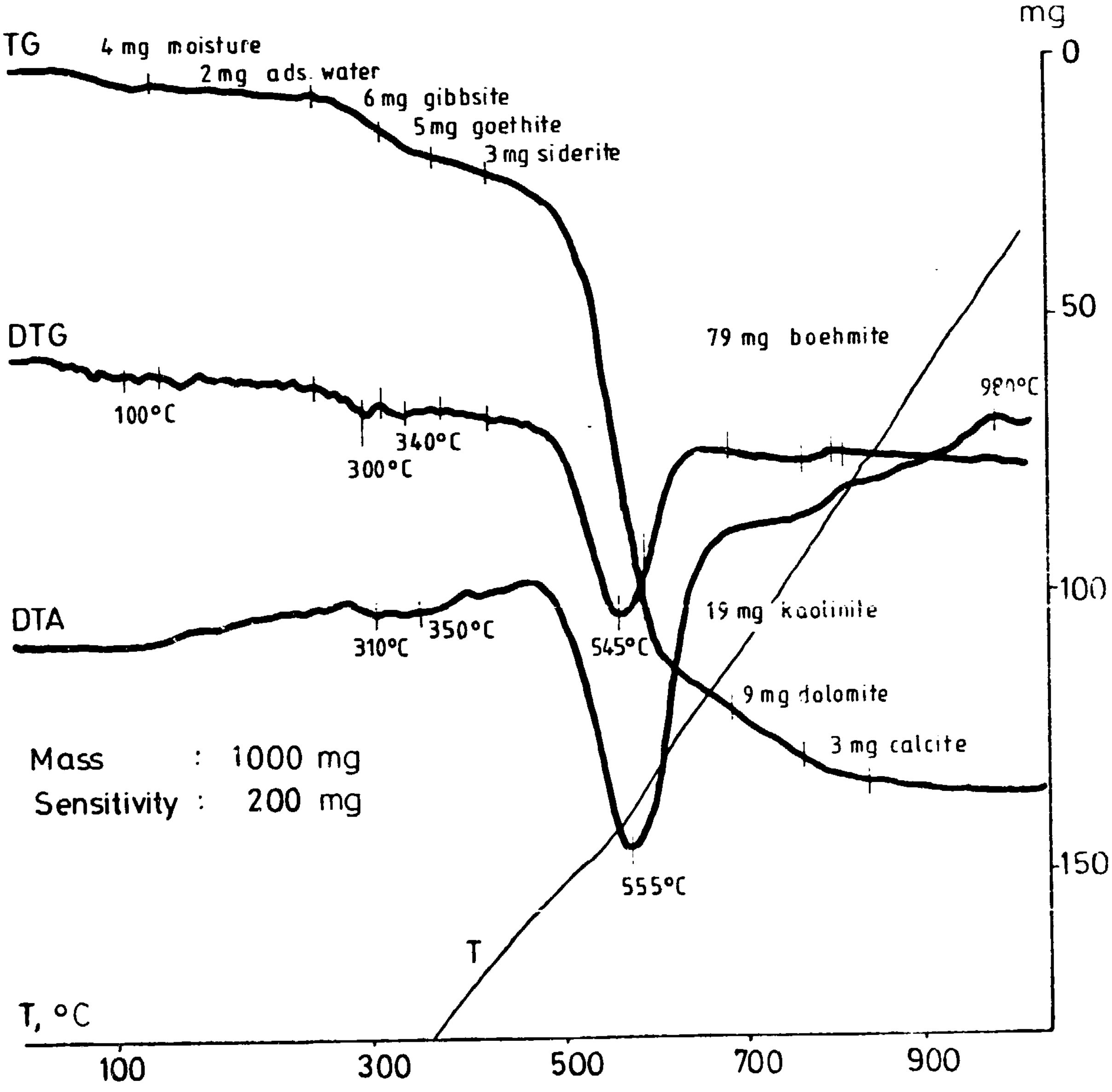

Fig.13. Derivatogram of a bauxite sample from Halimba region /Hungary/

Table 10. Phase analysis of a bauxite from Halimba region based on derivatography and chemical analysis

	L.O.I. %		Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	Phase
	H_2O	CO_2	%	%	%	%	%	%	%
Gibbsite	0.6		1.2						1.8
Boehmite	7.9		44.7						52.6
Kaolinite	1.9		5,4	6.3					13.6
Goethite	0.5				3.3				3.8
Siderite		0.3			0.7				1.0
Hematite					20.7^x				20.7
Titanoxides						2.5^x			2.5
Calcite		0.3					0.4		0.7
Dolomite		0.9					0.6	0.4	1.9
Adsorbed water	0.2								0.2
Total	11.1	1.5	51.3	6.3	24.7	2.5	1.0	0.4	98.8
Chemical analysis	12.8		51.5	6.3	24.7	2.5	1.1	0.4	99.3

x Calculated from chemical analysis

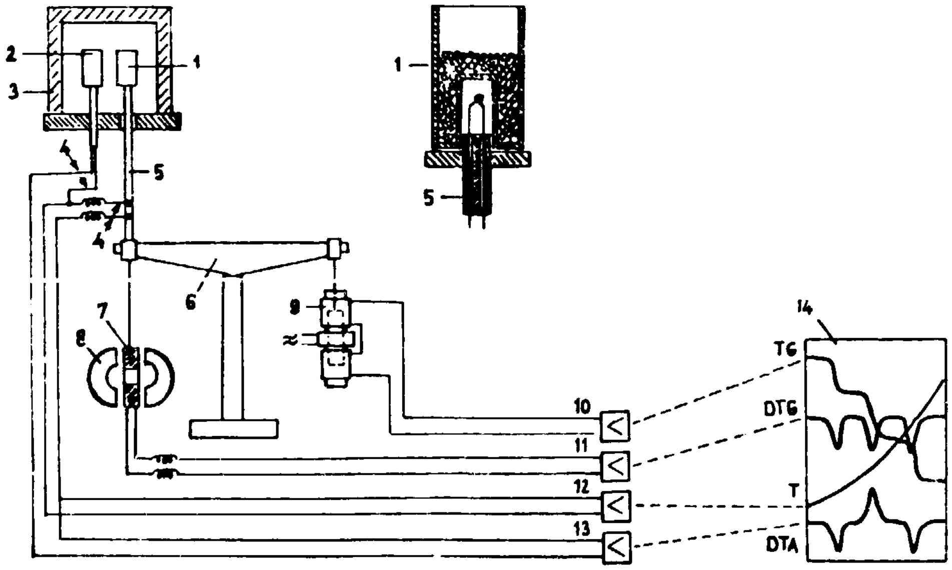

Fig.14. Scheme of a derivatograph

1 - specimen, 2 - inert material, 3 - furnace, 4 - thermocouples, 5 - ceramic tube, 6 - balance, 7 - coil, 10-13 - amplifiers, 14 - recorder

- Balance with the sample and the reference upwards, as well a coil downwards, the latter moving in the field of a permanent magnet on one arm, and a core of differential transformer on the other, for TG.

- Moter case with a.c. voltage stabilizer and toroid transformer to set heating rate by a novel program disc. Heating rate is also corrected according to DTA signal.

- Galvanometers converting currents of thermocouples, that of the moving coil and the differential transformer into mirror deflections.

Those are then recorded as T, DTA, DTG and TG signals, respectively, using parts of the light of a halogen lamp split and lead to the mirrors by optical fibers.

- Four channel recorder.

PROCEDURE

Switch on the derivatograph /type Q 1500/. Set the heating rate to 10°C/min, the starting voltage of the motor to 77 V /this value was determined by calibration measurements/.

Set the galvanometers free. Set the galvanometers to the following ranges: for DTA: 1/10 mV, for DTG: 1/15 mV, for T: 1000°C. Set sign "T" to 20°C on the recorder and zero the TG signal.

Put 1 g bauxite ground below 63 /um into one crucible on the arm and Al_2O_3 powder into the other crucible. The height levels must be equal in the two crucibles.

Lower the furnaces onto the crucibles. Set the balance free and wait for its neutral position, then set the DTG galvanometer free. Switch on the motors of recorder and of the writing heads.

Switch on heating and the motor of the program-disc. After about 100 mins, the derivatogram is completed.

Switch off the instrument, arrest the balance, lift up the furnace /a little/.

Evaluation of the derivatogram

Mark start, end and maximum rate point on DTA and DTG curves, determine their values in degrees using the special nomogram ruler.

Using peak temperatures in Table 9. identify phases in the bauxite sample. Project start and end point of DTG peaks onto TG curve.

Read the weight losses of individual phases off TG curve /in mg / and express values in percentages /sample mass: 1 g/.

Use formulae in Table 9. in calculating the quantitative mineral composition of the sample. Use data of chemical analysis and present data in form of a table similar to Table 10.

Compare result with results of X-ray diffraction /available in the laboratory/.

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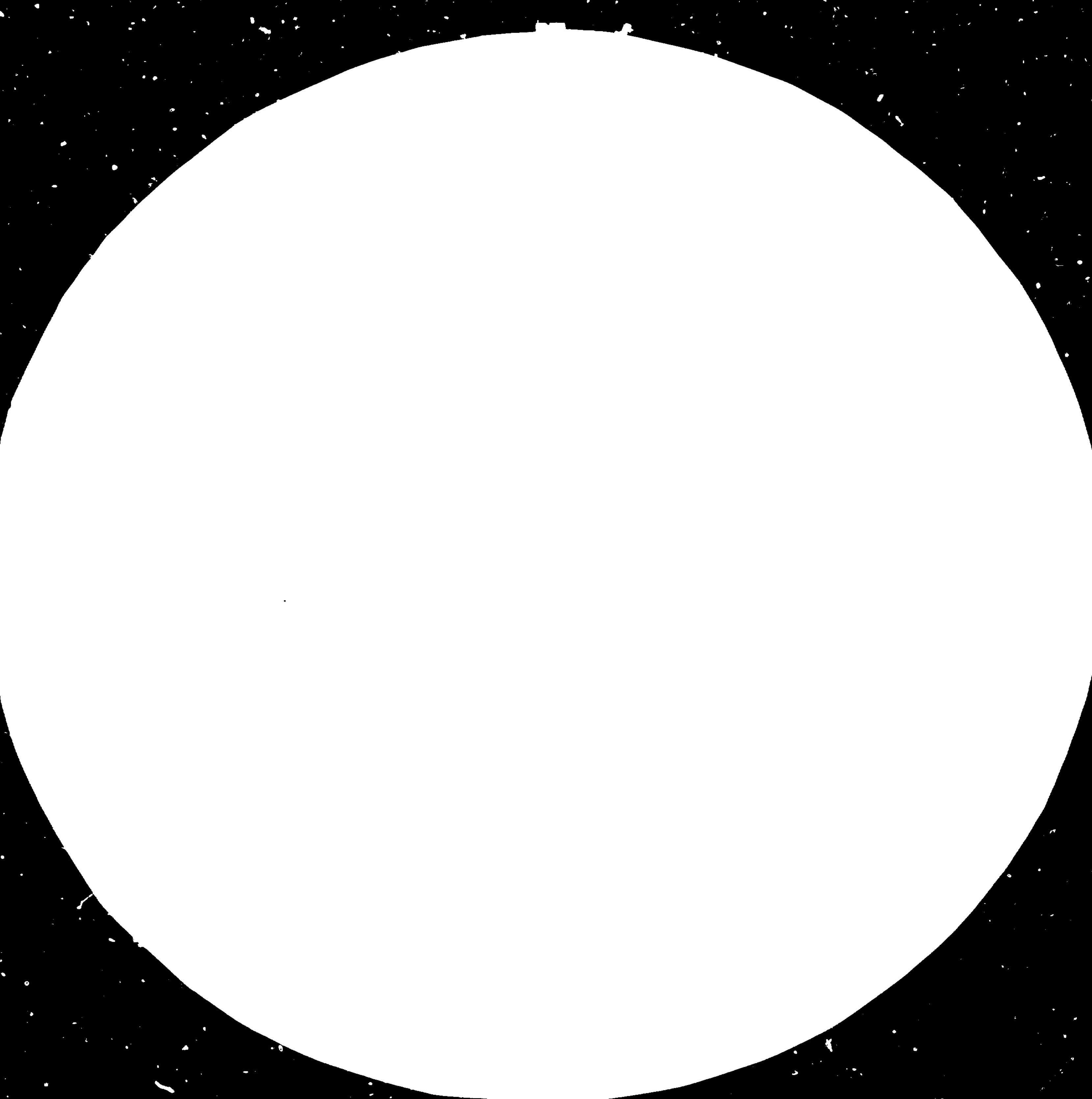

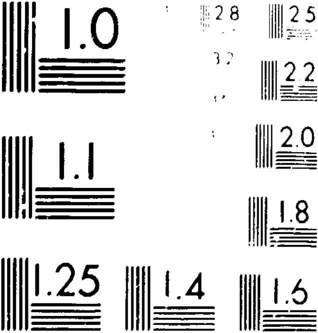
1.0
2.8
2.5
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

[illegible]

[illegible]

8. ELECTRON BEAM METHODS

PRINCIPLES

Electron beam investigations are based on the various types of interaction between the bombarding electrons and the material to get information about its morphology, structure and elemental composition. The most important and frequently used electron-material interaction processes are shortly discussed in this chapter.

In a scanning electron microscope /SEM/ a finely focused, high energy /from a few keV up to 50 keV/ electron beam scans over a selected area of the sample. Different types of particles are generated by the high energy electrons such as:

/i/ Backscattered electrons. Part of the bombarding electrons are scattered elastically /with no energy loss/ by the surface of the sample especially at high angles. Their intensity is proportional to the atomic number of the element present in the irradiated volume of the sample, i.e. the higher the atomic number of the element, the brighter the detail in the picture is.

/ii/ Secondary electrons emerge from the outer shells of the atoms of the sample due to the collision with the high energy bombarding electrons. They have relatively low energies /only a few eV/, thus they can escape only from a very thin /about 10 nm/ surface layer, consequently they can be used to image the surface of the sample. The protruding parts and edges of the sample, seem brighter in the secondary electron picture due to the greater number of electrons escaping from those parts than from cavities and holes.

/iii/ Transmitted electrons can be used for imaging and crystal structure determination of very thin samples /from a few tenth of a nm to a few hundred nm/.

/iv/ Auger electrons are applied for chemical analysis of the surface layer /a few atomic layers of thickness/.

/v/ Absorbed electrons are frequently used in semiconductor studies.

/vi/ The energy of the X-ray photons is characteristic of the elements emitting them. They come from a few μm thick layer of the surface; X-ray photons generated deeper are absorbed in the sample. Elemental distribution of an element of interest, line profile analysis and point analysis can be performed by detecting these photons. Elemental analysis by electron beam excited X-rays is often called microanalysis and the spectrometers are called microanalysers or microprobes. Energy dispersive microanalysers make use of solid state detectors, while microprobes apply crystal spectrometers. Qualitative elemental analysis can be made quantitative if the surface of the sample is flat and by using appropriate standard samples.

/vii/ Light photons are also generated by the high energy electrons in luminescent materials.

Morphological investigation of alumina hydrate

SEM in secondary electron mode gives valuable information about the morphological features of the alumina hydrate seed and product and helps to understand the mechanism of precipitation. It was found that alumina hydrates having the same grain size distribution curves may have different technological properties due to the different morphological features of the particles. Having studied a great number of alumina hydrate samples the investigation of the following features were proved to have importance:

character of grain size distribution, the minimum and maximum sizes,

shape and compactness of the alumina hydrate grains,

minimum and maximum length of the edges of individual crystals,

fine structure and defects of the individual crystals /e.g. irregular layered growth, etched pits, broken corners and edges, secondary crystals, etc./.

Recent impact of image analysers makes offers a quantitative characterisation of the size distribution and shape of alumina hydrate grains. However, it has to be mentioned, that by these systems the two-dimensional features can only be handled.

Investigation of morphology and elemental composition of bauxite

A scanning electron microscope supplied with an energy dispersive microanalyser makes it possible to study simultaneously the morphological features and the chemical composition of bauxites. On the basis of the studies carried out on different karstic and lateritic bauxites taken from all over the world the following morphological features were found to be of importance:

size and shape of the smallest resolvable details /they can be individual crystals and non-crystalline particles/,

space filling of bauxite. This feature relates to the porosity of the bauxite, i.e. there are big cavities and cracks in a loosely packed material and only small pores in a compact one,

size and shape of grains in the bauxite.

All these features depend on the age of the ore, on the temperature and tectonic pressure of the formation, consequently from the electron microscopic studies a lot of conclusions can be drawn on the circumstances of the formation of the bauxite.

By means of an energy dispersive microanalyser microvolumes and larger areas in the bauxite can be analysed. The investigation of elemental distributions of the main /Al, Si, Ti, Fe/ and impurity /Ca, Mg, S, P/ elements is of great importance in the technological evaluation of bauxite. All these elements can be distributed homogeneously or enriched in some textural features /like shells or crust of spherical grains, individual crystals of minerals/. For example, it is more favourable to have areas enriched with impurity elements than having a homogeneous distribution of them.

In some cases mineral identification of individual particles can be performed by investigating their morphology and by semi-quantitative energy dispersive microanalysis. Quantitative microanalysis of individual crystals can be made by an electron microprobe provided that particle size exceeds 5 µm of homogeneous composition.

EXPERIMENTAL

Electron beam methods always need high vacuum to make sure that electrons reach the sample and are not absorbed in the atmosphere. Another common feature of these methods that sample surface has to be made conductive to avoid undesirable charging effects.

Our SEM is a Philips SEM-505 type with about 6 nm resolution power in secondary electron mode. The most important parts of the instrument are as follow:

microscope column: contains an electron gun, an electron optical imaging and scanning system, a detector for secondary electrons: this is a photomultiplier with a collector plate, a detector for X-rays. The specimen holder is fixed to a goniometer which rotates, tilts and moves the sample.

The vacuum system is connected to the body of the microscope. This system contains oil-diffusion and rotary pumps to get and maintain about 6×10^{-3} Pa pressure inside the column.

By means of power supply and electronic units the microscope can be supplied with the appropriate accelerating voltage and the spot size of the beam can be set, further the brightness and the contrast of the cathode-ray tubes can be controlled.

The most important parts of the EDAX 711 energy dispersive microanalyser are as follows:

<u>the silicon detector</u>: kept at liquid nitrogen temperature permits accurate measurement of the very low currents generated by X-rays and reduce the dark current and thermal noise. The electric charge collected by the detector is very small, since X-ray photons produce only a few hundred electrons each. Whose height is proportional to the X-ray energy. Electronic devices produce a train of pulses whose height is proportional to the detector current.

These pulses are analysed by an <u>800-channel analyser</u>, which is connected to a cathode ray tube /CRT/ to display spectra.

On-line minicomputer /NOVA-3/12 with dual floppy/ performs data aquisition and data reduction on the spectra /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./.

A vacuum evaparator and a sputtering unit are used in the laboratory to cover the samples by a thin gold and/or carbon layer in vacuum.

PROCEDURES

Preparation of SEM samples of alumina hydrate and bauxite

Paint two copper sample holders with some "carbon black" conductive paint. Spread a small quantity of alumina hydrate powder over one of them covering the surface uniformly. Break of a piece of bauxite of 4-5 mm in size and put it on the second sample holder with the freshly broken surface upwards. Put the samples under the bell jar of the evaporator, put sharpened carbon rods between the two electrodes, then put a few mms of gold wire into the W basket. Cover the evaporator with the bell jar and pump the system to about 1 x 10^{-3} Pa. First evaporate carbon with 40 to 50 A, afterwards gold by about 30 A.

SEM + EDS of the prepared samples

Use the following parameters for morphological studies:
accelerating voltage: 25 kV,
spot size: 30 or 100 nm,
for making photographs: the number of lines /per frame/: 1000 or 2000, line time: 32 msec,
collector voltage of secondary detector: + 300 V.

First examine the sample on the TV screen, and look the most characteristic features of the bauxite and alumina hydrate sample, and take photographs with different magnifications.

In order to perform analysis by the energy dispersive microanalyser, use the following parameters:
accelerating voltage: 25 or 20 kV,
spot size: 500 nm /higher specimen current/,
counting rate: minimum a few hundred counts/sec, maximum 3000 counts/sec,
analysis time: 100 sec,
energy range: 0 - 16 keV.

First examine the sample on the TV screen looking for characteristic features of the bauxite. During analysis use the "Peak Ident." push-buttons for identification.

Switch on the computer /key switch/, put the supplied system diskette into the slot of the write hand diskette-drive. Load the operation system following the instructions available in the laboratory. When the analysis is ready, use the following commands: A1 /ENTER data from the multichannel analyser/, B1 /STORE spectrum on diskette/ and A6 /INTENSITY calculation of given elements/. Examine different parts of the sample and compare elemental composition of different particles.

9. SPECIFIC SURFACE AREA DETERMINATION BY GAS ADSORPTION METHOD

Principles

The specific surface area /SSA/ is an important characteristic of adsorbents, catalyst carriers, industrial fillers and abrasives.

In the alumina industry the magnitude of specific surface area of red mud can provide useful information about its settling, washing and filtration behaviour, the SSA of alumina hydrate is used to control precipitation process /seed charge/, SSA of alumina provides means for control the calcination process, grading the produced alumina for dry cleaning of fluorine containing gases.

The specific surface area of a solid is the sum of the external and internal surfaces by unit weight or unit volume.Their external surface is given by the sum of geometrical surfaces of grains, in the case of non-porous solids it can be calculated from the grain-size distribution curve provided that the shape /of the particles/ is known. The internal surface is the sum of pore surfaces, which depends on the quantity and size of pores contained in the material. It can be calculated from the pore size distribution curve. In highly porous solids, such as active charcoal, silica gel, zeolites, etc. the internal surface may be by orders of magnitude greater than the external surface.

For determination of SSA the phenomenon of physisorption is extensively used, whereby the sample is exposed to an inert gas atmosphere at a constant low temperature and the adsorbed gas quantity is determined by measuring the pressure variation due to the adsorption or desorption of a known volume of adsorbate /adsorption isotherm/.

During physical adsorption, gases are loosely bound to the surface of the solid in a molecular form by weak Van der Waals forces. A surface layer forms relatively quickly and is non-specific of the substance. The amount of gas adsorbed on the surface is reversibly dependent on pressure and temperature. For a given adsorbent - adsorbate pair:

$$v = f/T, p/,$$

where the functional form of f depends upon the properties of the adsorbent as well as of the adsorbate.

In the context of surface area determination, the best known theory of physisorption is that of Brunauer, Emett and Teller /1938/. By the introduction of a number of simplifying assumptions the BET theory provides an extention of the monolayer adsorption theory of Langmuir. Adsorption of the first layer is assumed to take place on an array of surface sites of uniform energy. Molecules in the first layer then act as sites for multilayer adsorption which in the simplest case, leads to the development of an infinite number of layers at the saturation pressure p_o. Under equilibrium conditions, the rates of condensation and evaporation are equated for each adsorbed layer. Summation of the amount adsorbed in all the layers then gives the BET equation:

$$\frac{p}{v/p_o-p/} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \cdot \frac{p}{p_o}$$

Apart from the pressure, p, the saturation pressure of the absorbate, p_o, and the volume of adsorbate, v, adsorbed at pressure, p, the above equation contains only two constants v_m, which stands for the volume of adsorbate representing a completely filled monolayer, and c, which is related exponentially to the heat of condensation.

The BET equation demands a linear relation between

$$y = \frac{p}{v./p_o-p/} \quad \text{and} \quad x = p/p_o.$$

Linearity of BET plots is restricted to a limited part of experimental isotherms - usually within the p/p_o range of 0.05 - 0.30. For this region, parameters, c and v_m can be determined from the slope and intercept of the y/x/ curve /see Fig.15/. Using those parameters, SSA can be calculated by the following formula:

$$SSA = S_o.v_m/w$$

where w is the weight of the specimen, S_o is a constant representing surface area covered by 1 cm^3 of adsorbate. /S_o for N_2 gas is 5.239 m^2/cm^3/.

The commonly used adsorbates are nitrogen, argon and butane. For determination of low surface areas /less than 1 m^2/g/ krypton is used due to its low vapor pressure. The adsorption process is more effective at low temperatures /cooling medium liquid nitrogen, solid CO_2 etc./.

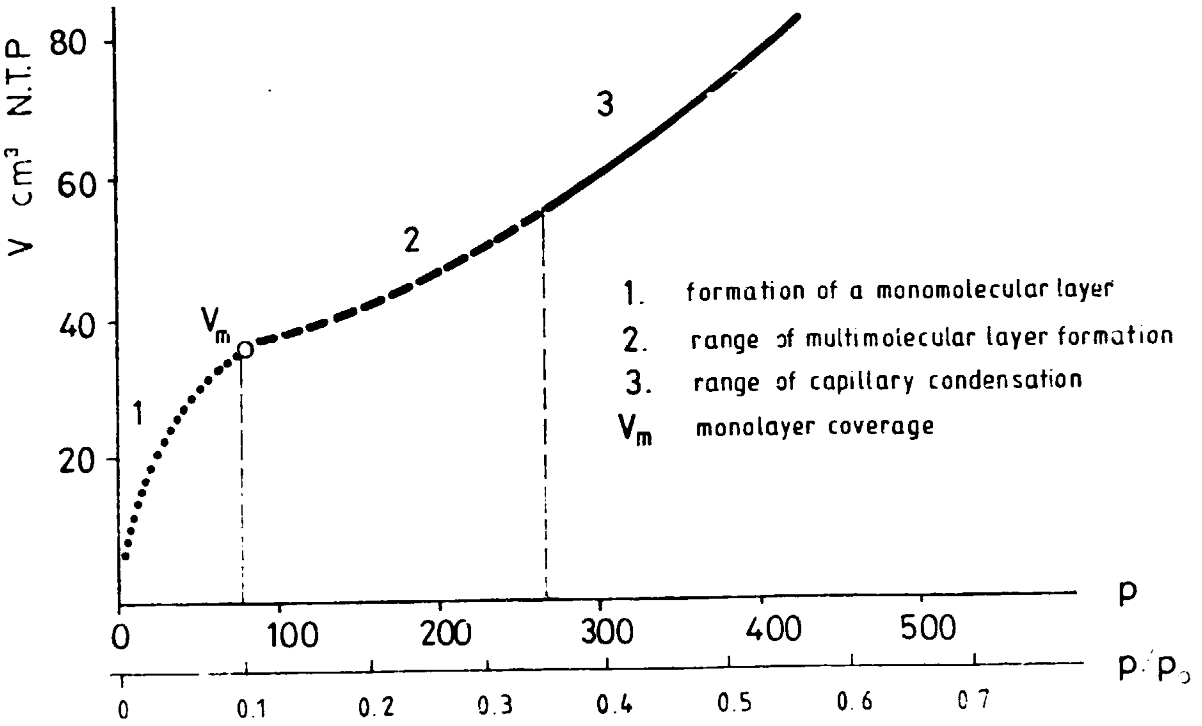

Fig.15. Nitrogen adsorption isotherm of Al_2O_3

Cleaning the surface of the sample from pollutants /adhesive water and gases adsorbed on the surface/ is essential before gas adsorption measurements, preferably without changing the structure of the sample.

EXPERIMENTAL

Instrument

The instrument used in laboratory practice is a sorptometer of type Sorptomatic 1800, made by Carlo Erba, Italy. It can be applied for the measurement of complete adsorption and desorption isotherms, it permits the determination of surface area above 1 m^2/g and pore size distribution in the range of 1,5 - 30 nm.

The adsorbate is high purity nitrogen, adsorption is measured at liquid nitrogen temperature /-196°C, 77 K/.

The instrument consists of the following main parts:
Sample tube,
Pipeline for admission /removal/ of the adsorbate,
Circuit for measurement and recording of equilibrium pressures,
Control circuit of liquid nitrogen level in the cooling bath,
Cycle programmer.

It can be operated either manually or automatically.

Sample preparation

Sample is cleaned in a so-called degassing unit in vacuum of 10^{-5} bar, at a temperature of 100°C /in the case of alumina/, for at least two hours.

PROCEDURE

Put sample tube with degassed sample into the instrument and pump it.

Fill the Dewar flask with liquid nitrogen.

Set pressure of the adsorbate /nitrogen/ with the pressure regulator.

Set volume of the admission chamber /normal - V_{s1}, reduced - $V_{s1/2}$, $V_{s1/4}$/ with the PISTON switch to $V_{s1/2}$.

Set the number of successive charges of the adsorbate.

Start the analysis by switching "MODE SELECTOR" to "ADS" position and "OPERATION MODE" to "PROGRAMMED" position.

The instrument operates automatically. Equilibrium pressures are printed out after each admission cycle. Data of the analysis are collected in a data sheet.

Calculate SSA values from the experimental data using a program on the TEXAS SR-59 calculator. The constants specific to the instrument used in the program are available from the instructor.

10. GRAIN SIZE ANALYSIS

PRINCIPLES

A powder is a mixture of grains of different dimensions and shapes. The size of a spherical or cubic particle can be characterized by one dimension, whereas a number of parameters are necessary to define irregular shapes.

The methods of grain size analysis - that is, finding the relative amount of grains of different sizes and statistically evaluating these data - may involve measurement of dimensions /direct methods/ measurement of sime other physical properties dependent upon the grain size /indirect methods/. The latter include measurement of parameters like change in electrical resistance, light absorption and scattering X-ray absorption, settling velocity etc.

The result of indirect methods are usually related to one or two derived diameters through appropricate models.

Direct methods

The most important direct methods are microscopy and sieve analysis.

In microscopy, particle size distribution is analysed by taking micrographs, in the range of 1 to 100 /um and 0.01 to 5 /um with optical and electron microscopes, respectively. Micrographs are statistically evaluated either by using calibrated nets or, more recently, image analysers. The latter is suitably for quantitative shape analysis.

Sieve analysis is the basic method of grain size analysis, which provides a distribution of the mean diameter, a distribution that suits physical reality the best. For elongated particles the minimum dimension is measured.

Sieve analysis is carried out with a set of sieves with openings following geometrical progression. To let the grains fall through the apertures, either the sieve set has to be moved mechanically, or the grains must be moved with some air or liquid stream.

Manual screening is used for coarse powders /500/um and above/.

Mechanical sieving may involve shaken screens or vibrating screens. They are suitable for medium and fine powders, respectively.

Air jet sieves are the most effective dry sieve analysers. Their range is 500 to 10 microns. In an air jet sieve, the dry sample is placed on the sieve. A rotating slot, with a length just below the sieve radius, blows an air jet which drives the grains upwards. Enough time given, all the particles that are small enough, fall through the sieve and are carried by the air stream to the collector. The analysis is carried out in the negative screen order, that is, the first sieve to be used is the finest and the residue of the sample is weighed for loss.

Wet screen analysing methods are used for fine and adhesive materials, or for materials being originally wet. Screening may be carried out manually or mechanically. The former is performed in the negative order. The latter imitates the corresponding dry screen methods. Wet mechanical screen may generally be applied to a lower limit of 25 microns, with ultrasonic vibrators down to 5 microns.

In a sedimentation test, settling rate /or time/ of particles, dispersed in a suitable medium is measured. If an irregularly shaped particle is allowed to settle in a liquid, its final velocity may be compared with that of a sphere of the same density settling under similar conditions. Mathematically, sedimentation is described by the movement of such model-spheres. This simple hydrodinamic model gives the formula for velocity of settling of a spherical particle as:

$$V_o = \frac{1}{18} \cdot \frac{d-\gamma}{\eta} \cdot g \cdot D^2$$

where:

V_o - velocity of settling /cm/sec/,

D - equivalent spherical diameter /the diameter of a sphere having the same velocity and density as the sample/,

d - density of the sample /g/cm^3/,

γ - density of the medium /g/cm^3/,

η - viscosity of the medium /poise/,

g - gravitational or centrifugal acceleration /cm/sec^2/.

This analysis is fast, because the grains - even the smallest ones - reach their final velocity in fraction of a second.

Assuming the hydrodinamic conditions laminar flow to be fulfilled even for the biggest particles, /Reynolds´ number, $R < 0.2$/ the Stokes approximation is good, and equivalent spherical diameters can be calculated. In this region during sedimentation, particles always move such a way, that the drag be of minimum. Thus, calculated equivalent spherical diameters are close to the minimum dimensions that can be calculated from sieve analysis.

Experimentally, settling rate can be determined by weighing /sedimentation balance/ or by measuring, for example, the light absorption of the suspension. The latter is called photosedimentation.

In this method, absorbance is measured as a function of time /settling time/ and height in the cuvette According to the Stokes formula thus, the bigger the particle, the earlier it settles. Lower regions get richer and richer in bigger particles.

At a certain height, the total light absorption is that of the individual particles left at that height.

This "complementary" information allows one to calculate cumulative particle size distribution.

Particle size analysers use a different principle. A very dilute suspension is made of the sample with some gas or liquid. The suspension is driven through a channel between the light source and the light detector in turbulent flow. As the particle passes the detector, the maximum absorbance of the light is detected /maximum dimension/.

There is an optimum solid to liquid/gas ratio, at which standard deviation of the particular fractions is minimum, because for concentrated suspensions multiple scattering take place, whereas at too low concentrations, statistical error is higher /see Fig. 16/.

Statistical evaluation of the particle sizes consists of plotting either cumulative, or relative percentage frequency curves as a function of grain size "classes". A further evaluation that helps characterizing particle size distribution by two-three parameter is to fit some distribution functions to these relative percentage distribution functions.

Depending on the symmetry of the distribution, normal /Gaussian/ lognormal or so called Rosin-Rammler functions are usually fitted to the curves.

The functional form of the

Rosin-Rammler distribution:

$$S_D = 100 \,.\, \exp/-(a/d)^b/,$$

lognormal distribution:

$$S_F = \left(\frac{100}{d.\sigma.\sqrt{2\pi}}\right)^d \cdot \exp\left(-\frac{/\ln d-a/^2}{2\sigma^2}\right) \cdot d$$

normal distribution:

$$S_N = \frac{100}{d.\sigma.\sqrt{2\pi}}^d \cdot \exp\left(-\frac{/d-a/^2}{2\sigma^2}\right) \cdot d$$

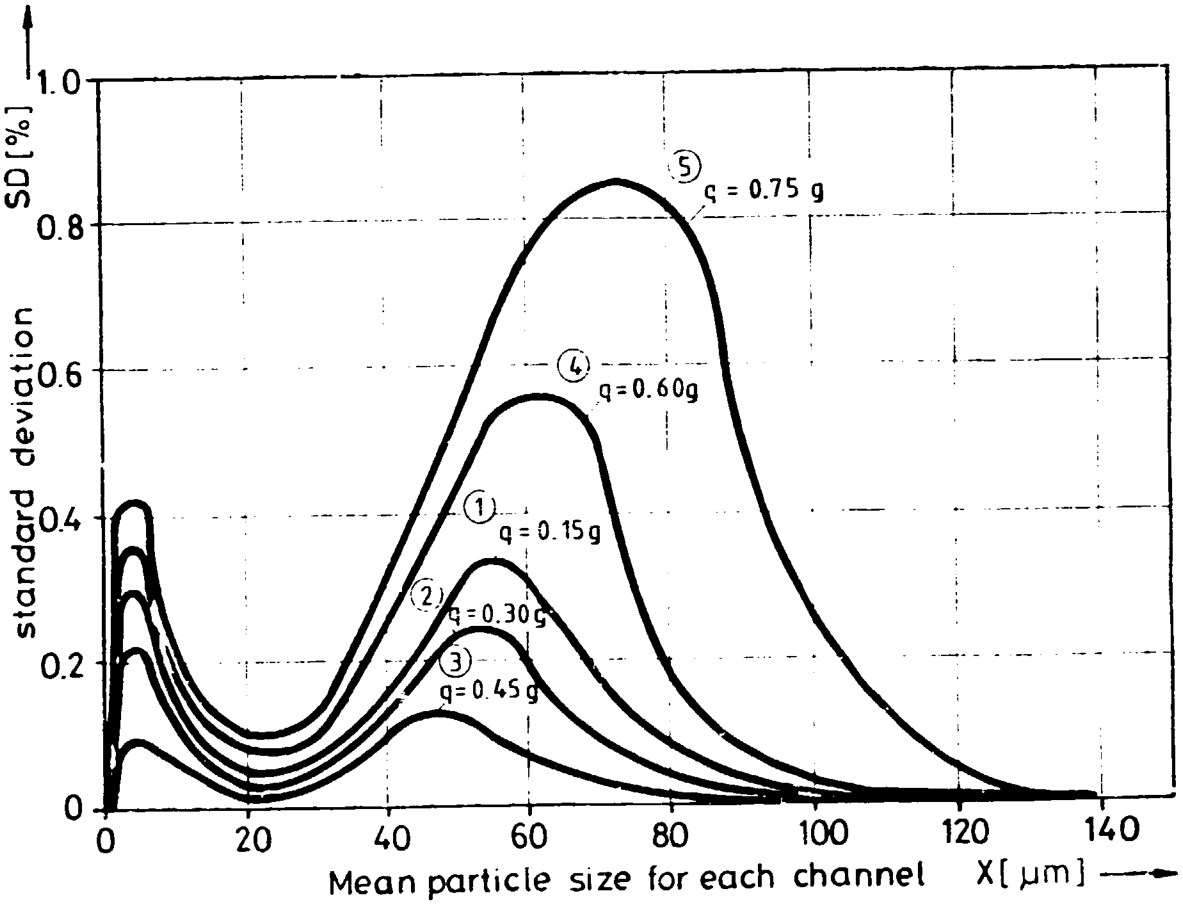

Fig.16. Trend of deviation for samples of different weight, using PA - 720

where

d - sieve opening or grain size,

a, b, σ - constants of the distribution.

Using these fitted parameters different methods can be compared on a double logarithmic plot. The different characteristic diameters "seen" by the different methods result in a parallel shift of the lines /see Fig.17/.

PROCEDURE

Take part on a demonstration of the operation of an Alpine A 200 LS air jet sieve.

Determine particle size distribution function for an alumina sample using fully automatic computerized Fritsch Analysette 20 photosedimentometer. Proceed as described in the User´s Manual. Type in"sample ident",and experimental parameters that are asked by the computer. Pour the sample into the cuvette and "start" the analysis. Parameters of the distribution function are automatically printed out.

Determine grain size distribution function of the same alumina sample by fully-automatic.

PA 720 particle size analyser. Proceed as described in the User´s Manual. Distribution function is automatically printed out.

Note: No sample preparation is necessary in either cases. Compare results of the two methods on a double logarithmic plot, similar to Fig.17.

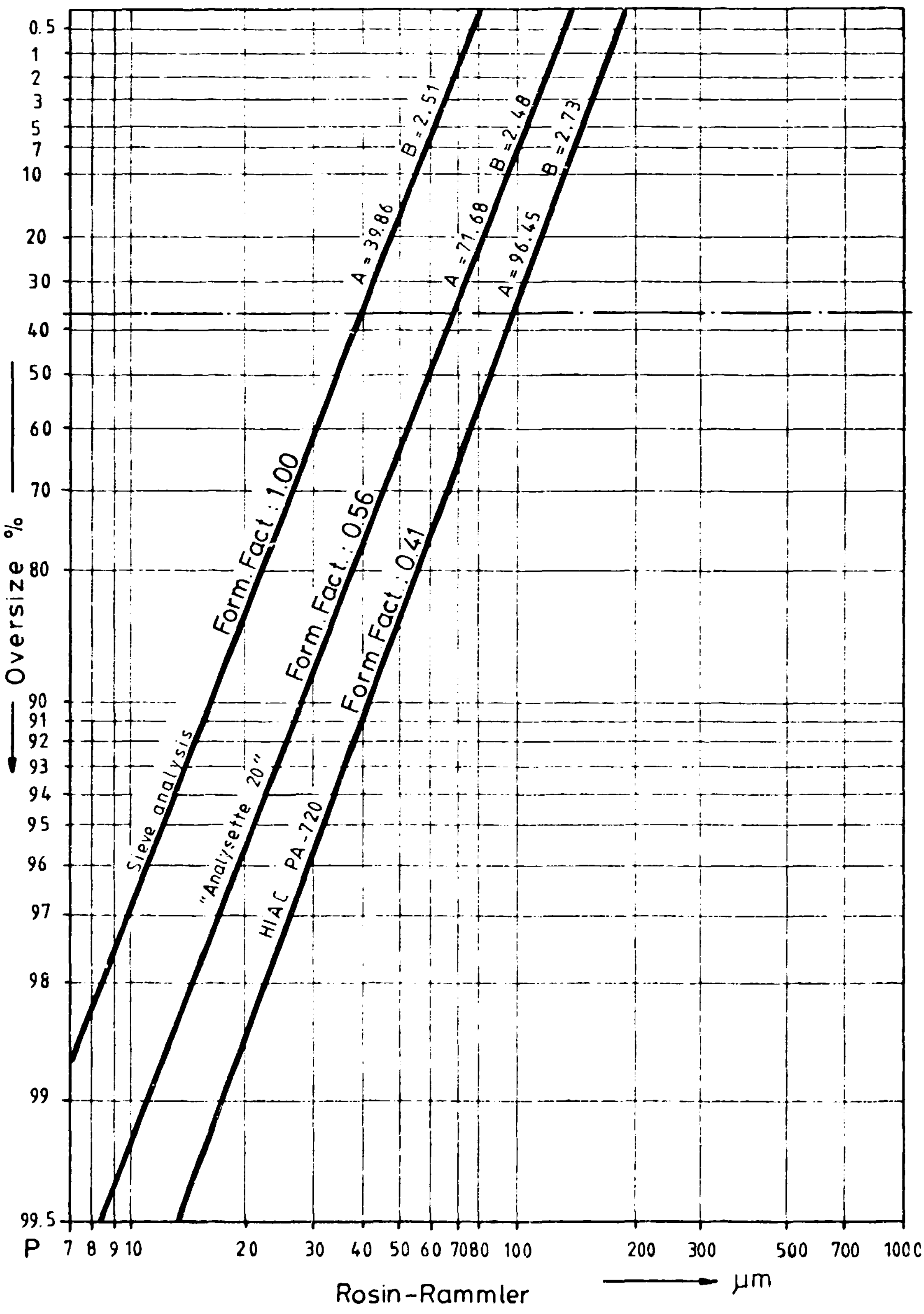

Fig.17. Comparison of analysis data in the RR diagram

11. PREDESILICATION OF BAUXITE

PRINCIPLES

In the Bayer process the treatment of bauxite with a caustic soda solution causes dissolution of silica as well as alumina. The silica in solution immediately begins to precipitate as a sodium-aluminium-hydrosilicate.

In plant operation the silica present in liquors is a source of problems listed below.

/i/ Scaling forms on the walls of pipes, preheaters, autoclaves evaporators etc. at many different points in the circuit.
/ii/ Significant amounts of soda and alumina are lost due to the formation of sodium-aluminium-hydrosilicates.
/iii/ Silica contaminates the alumina produced.

Predesilication in the Bayer-process means conversion of the reactive silica portion present in bauxite, into sodium-aluminium-hydrosilicate before the operation of digestion.

The aim of the predesilication operation is to keep the formation of scale at minimum - enabling dissolved silica to be precipitated before digestion,partly upon the easily cleanable surface of the predesilication tank partly upon mud particles. In this way the possibility of scale formation during subsequent process operations, is reduced.

Most of the sodium-aluminium-hydrosilicate, formed during predesilication, leaves the plant as a red mud component. It is almost insoluble in the digestion fluid.

Due to the long retention time predesilication procedure reduces the dissolved silica to an acceptably low level, decreasing also the degree of contamination of the alumina produced.

Silica in bauxite

Silica is a main component of different bauxite minerals. The so called unreactive silica appears in bauxite as quartz or rather as its polymorphic modifications: quartzite, opal, chalcedony.
The reactive silica portion is present as ingredient entering into the composition of different aluminium silicates: kaolinite, illite, dickite, halloysite, chamosite, pyrophyllite, allophane etc. All of them, with the exception of chamosite easily dissolve under conditions of predesilication. The dissolution of kaolinite is usually described by the equation:

$$Al_2O_3.2SiO_2.2H_2O + 6NaOH = 2NaAlO_2 + 2Na_2SiO_3 + 5H_2O$$

The structure of sodium-aluminate liquors containing silica

No theory has been supplied up to now in the literature concerning the structure of aluminate liquors, thus the crystallization mechanism of sodium-aluminium-hydrosilicates is not clear at present. However, different authors report the silica as being present in sodium-aluminate liquors in the following forms:

/i/ Na_2SiO_3

/ii/ complex anion $Al_6Si_6H_{12}O_{30}^{6-}$

or $Al_6Si_6H_{12}O_{30}Na_4^{2-}$

/iii/ Na_2SiO_3 and complex anion

$Al_2Si_2O_8/H_2O/_2^{2-}$

/iv/ Na_2SiO_3 and complex compound

$6Na_2O.8Al_2O_3.SiO_2.6H_2O$

/v/ complex compound

$mNa_2O.nAl_2O_3.2SiO_2$

It was also reported, that, after dissolution, silica is present as $SiO_2/OH/_2^{2-}$. This ion reacts with aluminate ions forming complex anions as follows:

$$SiO_2/OH/_2^{2-} + nAlO_2^- + aq \rightleftharpoons /SiAl_nO_{2/n+1/}OH/_m/^{/n+m/-} +$$

$$+ /2-m/OH^- + aq$$

These complex ions polymerize in the presence of Na^+ and H_2O and become nuclei for further crystallization.

The complex ions react also with Na^+ ions forming firstly amorphous, then crystallized sodium-aluminium-hydrosilicates:

$$2/SiAl_nO_{2/n+1/}/OH/_m/^{/n+m/-} + 2Na^+ + aq \rightleftharpoons$$

$$\rightleftharpoons /Na_2O.Al_2O_3.2SiO_2.n_1H_2O/ + 2AlO_2^- + aq$$

According to this explanation predesilication proceeds as follows:

/i/ formation of complex anions in solution /fast/
/ii/ formation of solid phase nuclei, polymerization /fast/
/iii/ growth of sodium-aluminium-hydrosilicate nuclei - crystallization and adsorption of ions from solution /slow - limits the velocity of predesilication/.

The nature of predesilication products

The structure and composition of sodium-aluminium-hydrosilicates formed in the process of predesilication depend upon temperature, concentration, molar ratio and presence of contaminants in the solution.

Although the formulae of the predesilication products reported in the literature vary significantly, the majority of the authors classify them as sodalites.

Predesilication product usually is a mixture of sodium-aluminium-hydrosilicates /sodalites, noselites, cancrinites, etc./ with various molar ratios of Na:Al:Si. These silicates can be characterized by the formulae of natural sodalites:

$$Na_2O.Al_2O_3.2SiO_2.0.33/Na_2,Ca/./2Cl,SO_4,CO_3,S_x,2AlO_2^-,2OH\ etc/.\ .nH_2O$$

Predesilication process

Predesilication is performed in Hungarian alumina plants at 95-105°C in tanks connected in series equipped with mechanical stirrers. The retention time is usually 6-10 hours.

Sodium-aluminium-hydrosilicates form in the slurry through the liquid phase in two steps from solid to solid. Therefore the reaction can be followed by determining the concentration of SiO_2 in the liquor or by measuring the Na_2O/SiO_2 molar ratio in the solid phase.

Fig. 18. illustrates the change of silica content in the liquid and the solid phases of the treated slurry during predesilication.

The silica content in the liquor first increases very fast, then decreases as sodium-aluminium-hydrosilicates separate from the solution; finally it reaches an equilibrium level.

The predesilication process can be characterized by its efficiency calculated from the solid phase analysis in a number of ways, e.g.:

$$\eta_1 = \frac{0.967 \cdot \frac{Na_2O}{SiO_2}}{0.67} \cdot 100\ \%$$

where: $0.967 \cdot \frac{Na_2O}{SiO_2}$ - molar ratio of Na_2O and reactive SiO_2 present in the predesilicated bauxite,

0.67 - molar ratio of Na_2O to SiO_2 in formed sodium-aluminium-hydrosilicate /sodalite/

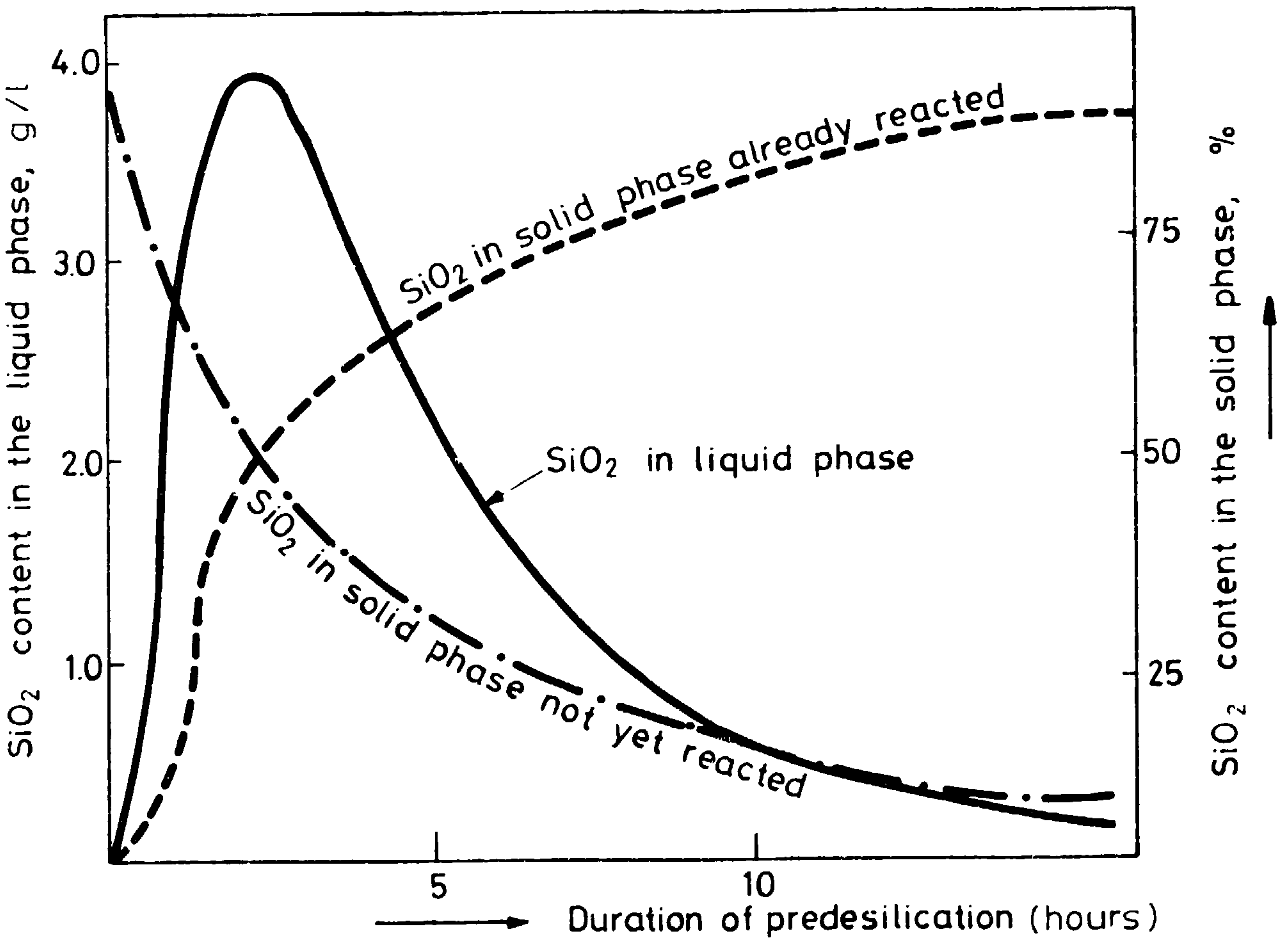

Fig.18. Variation of the silica content in the solid and liquid phases during the predesilication process

$$\eta_2 = \frac{Na_2O \cdot Fe_2O_{3bx}}{Fe_2O_3 \cdot SiO_{2rbx} \cdot 0.689} \cdot 100\ \%$$

where:

Na_2O - Na_2O content in the predesilicated bauxite,

Fe_2O_3 - Fe_2O_3 content in the predesilicated bauxite,

Fe_2O_{3bx} - Fe_2O_3 content of the bauxite to be processed,

SiO_{2rbx} - reactive SiO_2 content of the bauxite to be processed,

0.689 - weight ratio of Na_2O and SiO_2 in formed sodium-aluminium-hydrosilicate /sodalite/.

The predesilication efficiency can also be calculated from X-ray diffractometric phase analysis. This value can be defined as the ratio of SiO_2 in sodalite to the total reactive SiO_2 present in the bauxite before treatment:

$$\eta_3 = \frac{SiO_2 \text{ in sodalite}}{\text{total reactive } SiO_2} \cdot 100\ \%$$

The amount of SiO_2 contained in sodalite is equal to the difference between the total original reactive SiO_2 and the reactive SiO_2 left in the predesilicated bauxite in the form of soluble minerals - most frequently in kaolinite. In this case the amount of silica being present in the liquid phase is considered to have been just built in sodalite. Therefore the value of efficiency calculated in this way is higher than that of η_1 or η_2.

The amount of the reactive SiO_2 found in e.g. kaolinite is proportional to the integrated intensity of the kaolinite peak. This intensity can be determined from the X-ray diffractogram. For calibration the X-ray diffractogram of the untreated bauxite is taken. Using this relationship, the reactive SiO_2 left in the predesilicated bauxite as kaolinite can be calculated from kaolinite´s integrated intensity.

The other method of defining predesilication efficiency is based on quantitative IR spectrometry of kaolinite. The efficiency can then be calculated as:

$$\eta_4 = \frac{K_1 - K_2}{K_1} \cdot 100 \%$$

where:

K_1 - concentration of kaolinite in the untreated bauxite,

K_2 - concentration of kaolinite in the predesilicated bauxite.

To determine the concentration of kaolinite, one of its absorption peaks should be chosen in the IR-spectrum. Kaolinite absorption in the vicinity of wave number 3700 cm^{-1} is usually the least disturbed by the absorption of other phases in bauxite or red mud.

The absorbance A - according to Lambert-Beer´s law - is proportional to the component´s concentration.

$$A = E \cdot c \cdot d$$

where:

E - specific absorption coefficient,
c - component´s concentration,
d - thickness of the sample.

Keeping the amount of the samples constant for the purposes of predesilication, efficiency can simply be calculated from the formula:

$$\eta_4 = \frac{A_1 - A_2}{A_1} \cdot 100\ \%$$

where:

A_1 and A_2 are the absorbances of kaolinite in the untreated and in the predesilicated bauxite, respectively, measured at wave number of 3700 cm^{-1}.

If higher accuracy is required, absorbances should be corrected, according to the change in phase composition during predesilication, first of all to the concentration of iron.

Efficiencies η_3 and η_4 describe in fact solubility of kaolinite, while η_1 and η_2 characterize the predesilication process on the basis of the amount of formed sodium-aluminium-hydrosilicates. Therefore η_3 and η_4 are always bigger than η_1 and η_2.

Although none of the presented methods concerning calculation of efficiency are perfect, any of them may be used for characterization of predesilication.

PROCEDURE

Weigh in 40 g of bauxite into each of six digestion bombs and pour 150 ml of digestion liquor into each of them /the composition of both available from the instructor/. Place the bombs, safely sealed, into an oil bath preheated to 95°C.

Sample the bombs after 0.5, 1.0, 1.5, 2.0, 4.0 and 6.0 hours of holding. Separate liquid and solid phases of the samples by centrifuge.

Determine the following components of the liquid phase: $Na_2O_{caust.}$ cont. /gpl/, Al_2O_3 cont. /gpl/, SiO_2 cont. /gpl/, molar ratio. /Data available/.

Prepare predesilicated bauxite samples for the solid phase analysis as follows:

> wash each sample three times, each time using 300 ml of washing liquor /temperature: 95°C, $Na_2O_{caust.}$ conc.: 2 gpl/,
>
> dry the samples at 110°C, for 12 hours,
>
> grind the dried samples to obtain fine particles below 0.1 or 0.063 /um in size.

Using data of analysis /Fe_2O_3, SiO_2, Na_2O, loss on ignition/ calculate η_1 and η_2.

Follow the predesilication process as a function of time. Plot characteristic curves from data of the solid- and liquid phase analysis /data available/.

Evaluation of typical results of previous experiments

Calculate predesilication efficiency η_3 from X-ray diffraction data available from the instructor.

Calculate predesilication efficiency η_4 from IR spectrometric data obtainable from the instructor.

Compare η_3 and η_4 with corresponding values of efficiency calculated from chemical analysis.

Study the influence of varying conditions and concentrations of constituents in the predesilication process /solid content, $Na_2O_{caust.}$ concentration in liquor, temperature etc./ upon values of efficiency.

12. BAUXITE DIGESTION

PRINCIPLES

During digestion the aluminous minerals of bauxites are dissolved in form of sodium aluminate according to the following reaction equations:

$$Al_2O_3 \cdot 3H_2O + 2NaOH = 2NaAl/OH/_4$$
$$Al_2O_3 \cdot H_2O + 2NaOH + 2H_2O = 2NaAl/OH/_4$$

The digestion consists of the following partial processes:

wettening of the surface of minerals by the caustic solution,

surface interaction between the solid and liquid phases, dissolution of the solid,

saturation of the boundary layer between the solid and liquid phases,

diffusion of aluminate ions from the boundary layer into the liquor and of the reagent into the boundary layer.

At given digestion parameters the following equation was proposed by Korcsmáros for description of the process:

$$\frac{dc}{dt} = \frac{D}{r} \cdot S \cdot /c_t - c/ \cdot /c_1 - c/,$$

where

c - Al_2O_3 concentration in the liquor /kmole m^{-3}/,

c_t - Al_2O_3 concentration in the liquor in case of total dissolution of the Al_2O_3 content soluble by a given digestion technology /kmole m^{-3}/,

c_1 - equilibrium Al_2O_3 concentration in the liquor /kmole m^{-3}/,

D - diffusion coefficient of the aluminate ions /m^2 s^{-1}/,

r - thickness of the diffusion layer /m/,

S - characteristic surface for material transport of the aluminous minerals /m^2 $kmole^{-1}$/.

The digestibility of the bauxite is influenced by factors like the chemical and mineralogical composition, textural and morphological properties of the ore, such as degree of crystallinity of the aluminous minerals, the size of individual crystals, etc.

From the point of view of digestibility the mineral form of the aluminium content is of primary importance. The most frequent aluminous minerals of bauxite in the order of decreasing digestibility are the following:

gibbsite: $Al_2O_3.3H_2O$
boehmite: $Al_2O_3.H_2O$
diaspore: $Al_2O_3.H_2O$

Gibbsitic bauxites can be digested at 105°C at relatively low /100-140 g/l k Na_2O/ caustic concentration. For digestion of boehmitic bauxites digestion temperature of 200-240°C and higher /180-240 g/l k Na_2O/ caustic concentration are needed, while for diasporic bauxites 240-260°C and CaO additive are necessary for an appropriate efficient digestion. In case of the different aluminous minerals the saturation concentration of Al_2O_3 or the equilibrium caustic Na_2O/Al_2O_3 molar ratio in the liquor are different, too. In Fig.19. the attainable equilibrium Na_2O/Al_2O_3 molar ratios at the dissolution of gibbsite, boehmite and diaspore, respectively, are plotted versus the caustic liquor concentration and the digestion temperature.

According to recent investigations the bauxites having the same mineral composition but originating from different deposits, may have different digestibility, too, due to the different degree of crystallinity.

The smaller are the individual crystals, the larger the interface between the solid phase and the liquor, and consequently the higher the digestibility is.

The influence of bauxite texture is also important. Porous, loosely packed bauxites can be more easily digested than compact ones. The digestibility of aluminous phases is highly impeded by oolitic structure occurring in some deposits, whereby aluminous minerals are surrounded by ferrous crust, or aluminium and iron rich shells alternate.

Besides the aluminous minerals - in simultaneous and consecutive reactions - other minerals of bauxite also react with the liquor causing Al_2O_3 and NaOH losses. Some reaction products are accumulated in form of dissolved salts in the Bayer circuit.

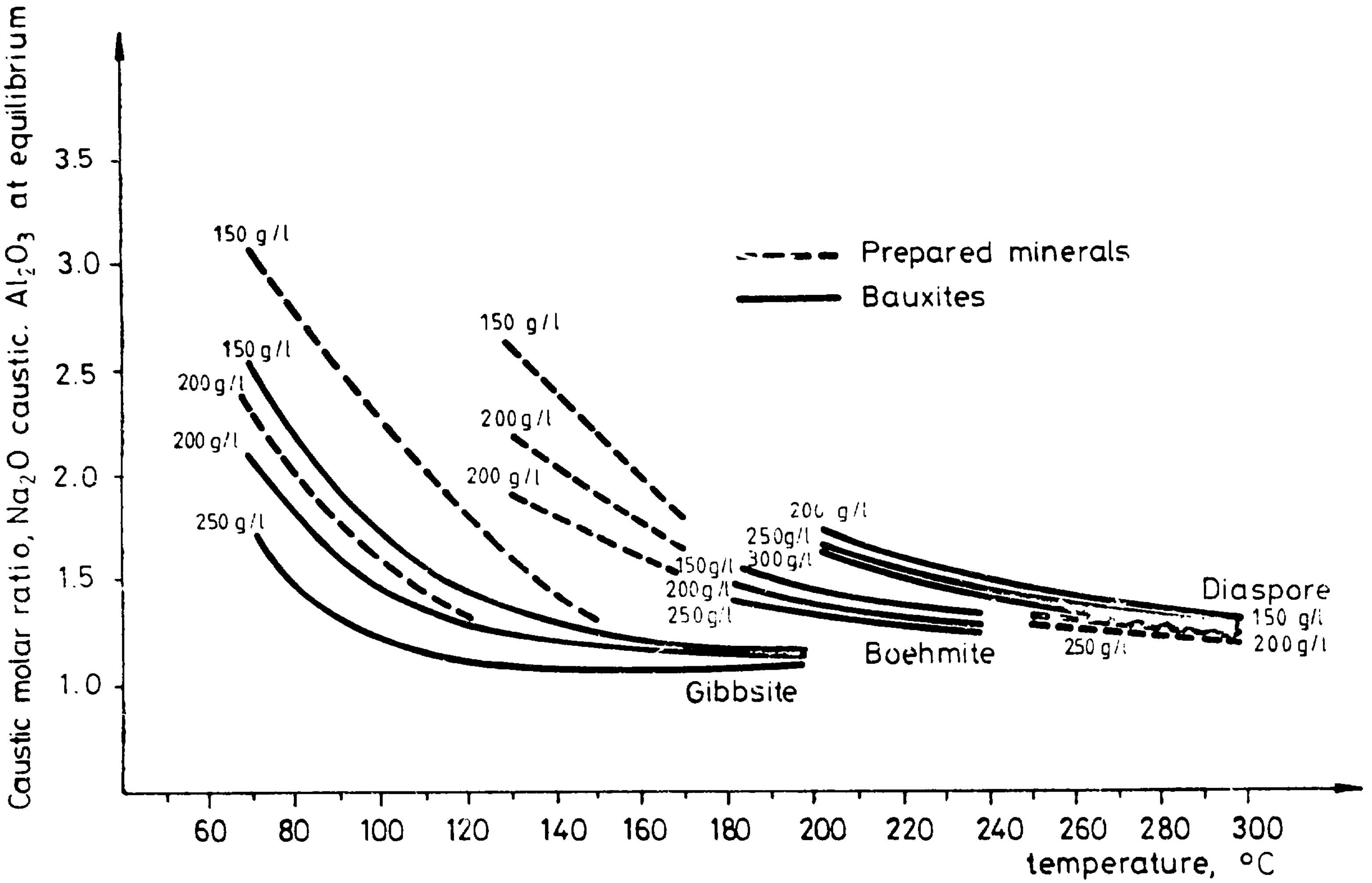

Fig.19. Equilibrium caustic molar ratio during digestion of bauxites of different mineralogical composition

The objective of a laboratory digestion test

Dissolution of the maximum amount of aluminous minerals from the bauxite is essential from the point of view of the efficiency of the Bayer technology, consequently, the digestion technology should be optimized by laboratory tests and fitted to the particular ore.

Characteristic curve of digestion

During the technological evaluation of the bauxite the following studies should precede digestion test: chemical analysis, qualitative and quantitative mineralogical investigation and morphological studies. Knowing the mineralogical and textural properties of the given bauxite, the number of the digestion tests can be restricted to the range near to the expected optimum conditions.

Knowing the mineralogical composition of the bauxite, /gibbsitic, boehmitic or diasporic/ and on the basis of practice and literature - the optimum digestion temperature and caustic liquor concentration can be determined /see Fig.19/. The most important task left is to determine the optimum bauxite - caustic liquor ratio i.e. the caustic Na_2O/Al_2O_3 molar ratio after digestion.

Note: In the American practice the composition of the liquor is usually characterized by the so called A/C ratio which is defined as the weight ratio Al_2O_3/caustic Na_2CO_3.

From economic points of view the maximum liquor saturation should be used, whereby the aluminous minerals reasonably dissolve, too. This optimum bauxite-liquor ratio can be determined by constructing the so called characteristic digestion curve. To construct this curve 5-6 digestion tests are performed at different bauxite - caustic liquor ratio and the Al_2O_3 yield is plotted versus caustic Na_2O/Al_2O_3 molar ratio /or A/C ratio/ measured in the liquor after digestion. Using this characteristic curve the lowest caustic Na_2O/Al_2O_3 molar ratio /highest A/C ratio/ can be chosen which ensures the maximum efficiency of digestion.

Calculations of technological parameters

The amount of bauxite necessary to achieve the planned molar ratio after digestion taking the expected NaOH and Al_2O_3 losses into account can be calculated on the basis of caustic solution and bauxite analysis data:

$$G = \frac{c_k/\alpha_0 - \alpha_a/}{\alpha_0 . 0.608 . \alpha_a/A-S/+\alpha_0 . 0.608\ S}$$

where:

G - the mass of bauxite necessary to 1 liter caustic liquor /kg/,

c_k - k Na_2O concentration of digestion liquor /g/l/,

α_0 - k Na_2O/Al_2O_3 molar ratio of digestion liquor,

α_a - planned molar ratio after digestion,

A - Al_2O_3 content of the bauxite /g Al_2O_3/kg bauxite/,

S - SiO_2 content of the bauxite /g SiO_2/kg bauxite/.

Calculation of Al_2O_3 recovery

Knowing the chemical composition of the bauxite and red mud, Al_2O_3 recovery of digestion is calculated by the following formula:

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

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

Fe_2O_3 and Al_2O_3 content of the bauxite /bx/ and red mud /m/, in w % are in brackets.

Calculation of the Na_2O/SiO_2 molar ratio

The Na_2O/SiO_2 molar ratio characteristic for the bound soda losses can be calculated as follows:

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

% wpct of red mud.

The specific bauxite consumption can be determined by the following formula:

$$Q = \frac{990}{\eta' a} \quad /t/t \text{ alumina}/,$$

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.

The quantity of the produced red mud for the production of 1 t alumina is the following formula:

$$G = Q \cdot \frac{(Fe_2O_3)_{bx} \, \%}{(Fe_2O_3)_m \, \%} \quad /t \text{ mud}/t \text{ alumina}/$$

where:

bx - bauxite,

m - red mud.

By means of the laboratory digestion tests a digestion technology should be chosen which ensures maximum Al_2O_3 yield at minimum energy consumption and minimum NaOH loss.

Favourable settling properties of the red mud are also of great importance.

A particular technology should rely on optimal values of
digestion temperature,
caustic liquor concentration,

holding time,
Na_2O/Al_2O_3 molar ratio in the liquor after digestion,
optimum amounts of digestion additives /for example CaO in case of diasporic bauxites/,
achievable Al_2O_3 yield in case of optimum digestion parameters,
expectable amounts of bound NaOH losses,
rate of dissolution of impurities.

In some cases the aim of laboratory digestion tests is to produce red mud for other laboratory investigations /red mud settling, causticization tests/.

EXPERIMENTAL

Equipment

In Fig. 20. an oil bath digester supplied with controlled electric heating and six steel autoclave bombs of 200 ml are shown. In this oil bath digester applicable in the temperature range between 100°C and 260°C the autoclave bombs can be rotated by a speed of 18-20 rev/min to ensure the stirring of the bauxite slurry. To digest larger amount of slurry, 4-5 or 10 l, electrically heated, mechanically stirred autoclaves can be used, as shown in Fig. 21.

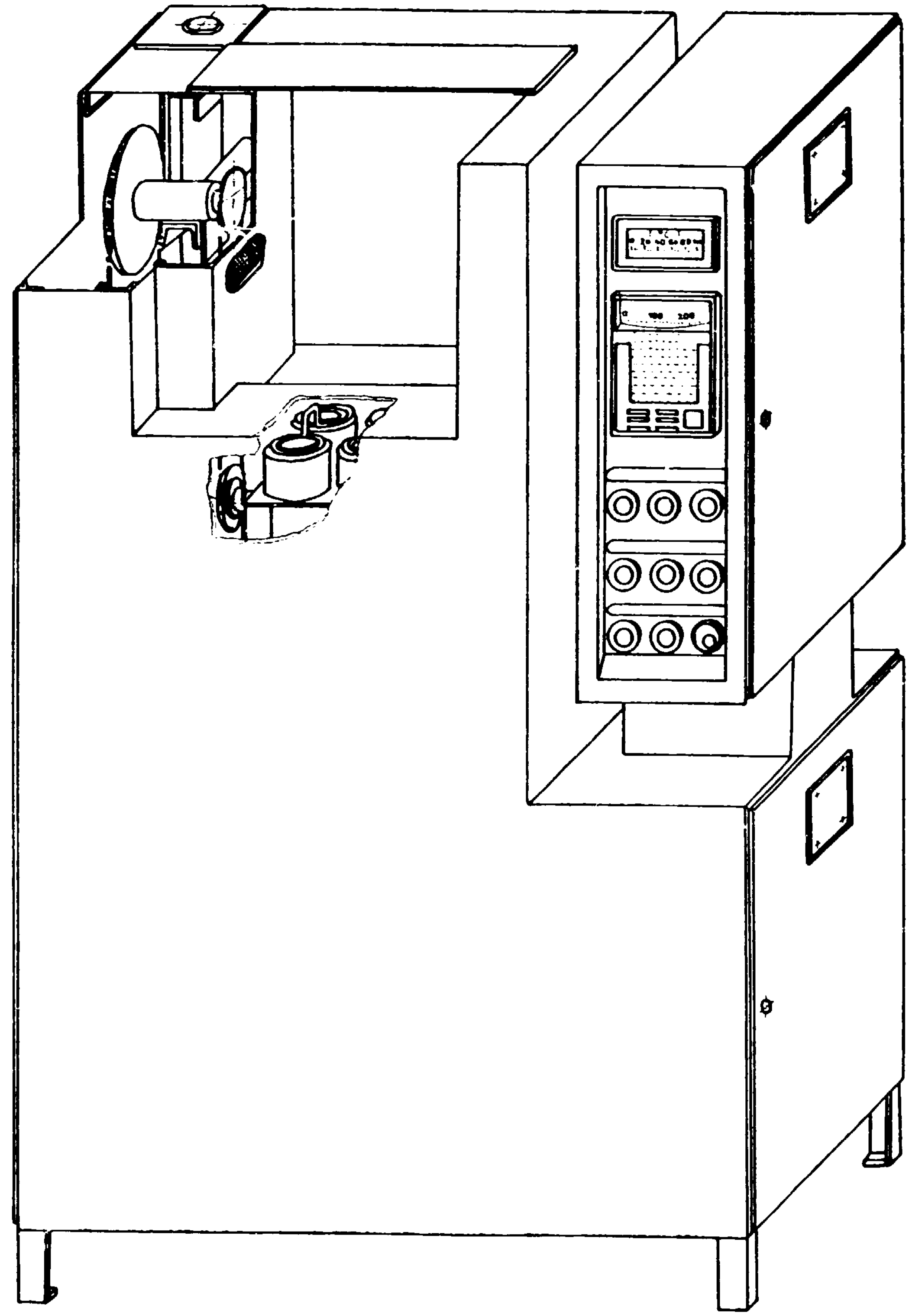

Fig.20. Oil bath equipment for digestion

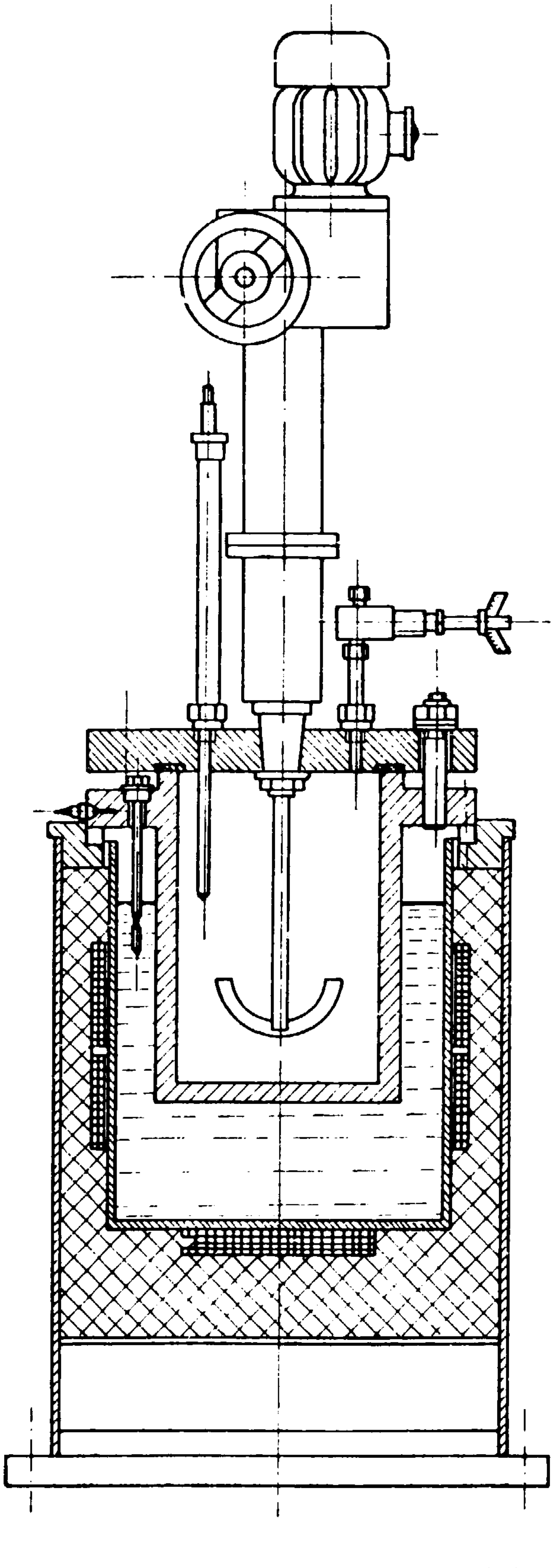

Fig.21. Laboratory autoclave supplied with mechanical stirrer

Materials

The representative bauxite sample is ground below 320 /um and homogenized carefully. Plant caustic solution with all the organic and inorganic impurities is used. In shortage of such plant liquor synthetic sodium aluminate solution of appropriate concentration and Na_2O/Al_2O_3 molar ratio can be made by dissolving aluminium chips in NaOH solution.

PROCEDURE

Weigh the bauxite necessary to six digestion tests according to the following kNa_2O/Al_2O_3 molar ratios: 1.2, 1.3, 1.4, 1.6 and 1.8. The volume of digesting liquor is 150 ml in each case.

Switch on the oil-bath digester and heat it up to 100°C, pour 150 cm^3 of digesting liquor of given concentration in each of autoclave bombs. Add the quantity of bauxite to the digestion liquor, charged in order of increasing molar ratio /decreasing weight of bauxite/. Then stir the suspension well with a glass rod.

Put the sealed autoclave bombs into the oil-bath and fix them well, switch on the rotator and start heating the bath to the required digestion temperature. Having attained the required digestion temperature, carry on digesting the bauxite for 20 minutes /gibbsitic bauxite/, for 60 minutes /boehmitic and diasporic bauxite/. When you went to finish digestion, switch off the rotator, take the autoclave bombs out of the bath. 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 out 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 the last washer in the red mud 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 the caustic wash liquor away.

Repeat the repulping and centrifugation three times, put the separated red mud into a drying oven and dry overnight at 110 deg.C.

Prepare and grind the red mud minus 100 µm for chemical analysis and minus 63 µm for X-ray diffractometry.

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, CaO, MgO.

Chemical analysis and X-ray diffraction data of earlier tests can be used for calculations. On the basis of the chemical composition of the bauxite and red mud, calculate the Al_2O_3 recovery in all the six experiments.

Construct the characteristic curve of digestion plotting η values as a function of /Caust. $\underline{Na_2O}/\underline{Al_2O_3}$/ molar ratio in aluminate liquor /European Bayer/, and as a function of /Al_2O_3/caust. $\underline{Na_2CO_3}$/ weight ratio in aluminate liquor /American Bayer/, respectively.

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

Calculate the $\underline{Na_2O}/\underline{SiO_2}$ molar ratio characteristic for the bound soda losses using the appropriate formula /see PRINCIPLES/.

Calculate specific bauxite consumption and red mud production.

13. ALUMINA HYDRATE PRECIPITATION

PRINCIPLES

Alumina hydrate precipitation is the decomposition of a supersaturated sodium aluminate solution in the presence of seed crystals according to the following reaction equation:

$$\mathrm{NaAl/OH/_4} \rightleftharpoons \mathrm{Al/OH/_3} + \mathrm{NaOH}$$

During precipitation of alumina hydrate the solution is approaching an equilibrium state. In practice, 50-55 % of aluminium can only be precipitated from the solution.

The structure of the sodium aluminate solution and the details of the decomposition have not yet cleared up. On the basis of physical and physico-chemical investigations it was concluded by Hungarian researchers that in a certain composition-, concentration and temperature range complicate aluminate complexes are formed by the polymerization of $\mathrm{Al/OH/_4^-}$ ions. These complexes are in equilibrium with each other in the following hydration-dehydration processes:

$$\begin{tikzcd}
\mathrm{Al/OH/_4^-} \arrow[r, shift left, "+\ \mathrm{OH}"] \arrow[d, shift right, "-\ \mathrm{H_2O}"'] & \mathrm{Al/OH/_4.OH} \arrow[l, shift left, "-\ \mathrm{OH}"] \\
\mathrm{Al_2O/OH/_6^{2-}} \arrow[u, shift right, "+\ \mathrm{H_2O}"'] \arrow[r, shift left] \arrow[d, shift right, "-\ \mathrm{H_2O}"'] & \mathrm{Al_2O/OH/_6^{2-}.OH^-} \arrow[l, shift left] \\
\mathrm{Al_6O_n/OH/_{24-2n}^{6-}} \arrow[u, shift right, "+\ \mathrm{H_2O}"'] \arrow[r, dashed] & \mathrm{Al/OH/_3}
\end{tikzcd}$$

Consequently decomposition of the solution and precipitation of alumina hydrate can be described as follows:

$$Al/OH/_4^- \xrightarrow{-H_2O} Al_2O/OH/_6^{2-} \xrightarrow{-H_2O} Al_6O_n/OH/_{24-2n}^{6-} \xrightarrow{-OH^-} Al/OH/_3$$

Crystallization consists of the following processes:

/i/ the growth of seed crystals,
/ii/ secondary nucleation, formation of new particles,
/iii/ agglomeration, cementation of the seed crystals into composite grains,
/iv/ fragmentation, attrition of the bigger crystalline grains due to the friction effect on stirring.

During the precipitation of alumina hydrate two requirements must be fulfilled:

/i/ to make precipitation as efficient as possible,
/ii/ to produce an alumina with grain size distribution and physical properties suitable for aluminium smelting.

Decomposition of the sodium aluminate solution and alumina hydrate precipitation can be highly influenced by varying parameters such as liquor concentration, initial Na_2O/Al_2O_3 ratio, seed quantity, precipitation temperature, etc.

Precipitation efficiency is unfavourably influenced by the organic and inorganic impurities present in the Bayer process. The aim of the laboratory precipitation tests is to investigate the influence of the precipitation parameters and the effects of different impurities.

The most important methods used for characterization the seed and the product are as follows:

grain size distribution by sieve analysis or photosedimentometry,

determination of specific surface area by BET method,

investigation of the morphological features by scanning electron microscopy,

attrition tests to evaluate the stability of crystalline aggregates and agglomerates.

Modelling the precipitation process

Precipitation of alumina hydrate does not strictly depend on the quality of the processed bauxite, so the laboratory precipitation tests do not belong to the technological evaluation of bauxites. The basic parameters of precipitation are standardized in both the American and European Bayer technologies. Laboratory precipitation tests are usually directed to help solving certain plant operational problems or studies of the kinetics and mechanism of the precipitation.

Precipitation is difficult to modell in the laboratory because cooling rate and hydrodinamic conditions of plant precipitation are difficult to reproduce and they have a considerable influence on the crystallization. An additional difference is that the alumina hydrate seed stored in the laboratory can grow old and become inactive.

Taking these difficulties into consideration a perfect reproduction of plant conditions is far beyond a laboratory model test of precipitation. However, comparative laboratory experiments are important on well defined conditions. These comparative tests are made either isothermally or according to a given cooling program.

Calculation of the seed quantitiy

The seed quantitiy is characterized by the so called seed ratio:

$$S_R = \frac{A_S}{A_L} ,$$

where:

A_S - the Al_2O_3 content of alumina hydrate used for seed /g or kg/,

A_L - the Al_2O_3 content of sodium aluminate solution /g or kg/,

S_R - seed ratio.

The mass of wet seed corresponding to a given seed ratio is calculated by the following formula:

$$G_S = A.S_R.k.\frac{100}{100-M} ,$$

where:

G_S - the mass of wet alumina hydrate needed for 1 liter sodium aluminate solution /g/,

A - initial Al_2O_3 concentration in sodium aluminate solution /g/l/,

S_R - seed ratio,

k - $Al_2O_3.3H_2O/Al_2O_3$ molar ratio,

$$k = \frac{156\ g}{102\ g} = 1,53$$

M - the adhesive moisture of seed /%/.

Calculation of precipitation efficiency

The precipitation efficiency attained until the sampling is calculated by the following formula:

$$\text{Efficiency} = \frac{A_s - A_t \frac{c_s}{c_t}}{A_s} \cdot 100 \quad /\%/$$

where:

A_s - starting Al_2O_3 concentration in the solution /g/l/,
A_t - Al_2O_3 concentration at the sampling /g/l/,
c_s - starting Na_2O concentration in the solution /g/l/,
c_t - k Na_2O concentration at the sampling /g/l/.

Taking into account that the caustic molar ratio of the solution is inversely proportional to the Al_2O_3 content in the solution, the precipitation efficiency can be determined by the following formula, too:

$$\text{Efficiency} = \frac{M_t - M_s}{M_t} \cdot 100 \quad /\%/,$$

where:

M_s - caustic molar ratio of the starting solution,
M_t - caustic molar ratio at the time of sampling.

Plotting the precipitation efficiency versus the time, the so called precipitation curve is gained.

EXPERIMENTAL

Apparatus

A laboratory precipitation equipment is shown in Fig.22. Precipitation bottles supplied with mechanical stirrer and a cover are immersed into a thermostat which is controlled by temperature controller. Depending on the number of bottles, 6-12 tests can be performed in parallel. Laboratory model of an air-lift agitated tank of 25 l is shown in Fig.23.
Such type of equipment can be useful in a plant laboratory where the materials necessary to the tests are available.

Autoclave bombs rotating in a thermostat can also be used, for precipitation tests. The agglomeration phenomena are usually investigated in such type of equipment.

Materials

In laboratory tests, plant sodium aluminate solution with all the organic and inorganic impurities and fresh plant seed are generally used. If plant liquor of appropriate molar ratio is not available, the required solution can be made by dissolving calculated quantity of

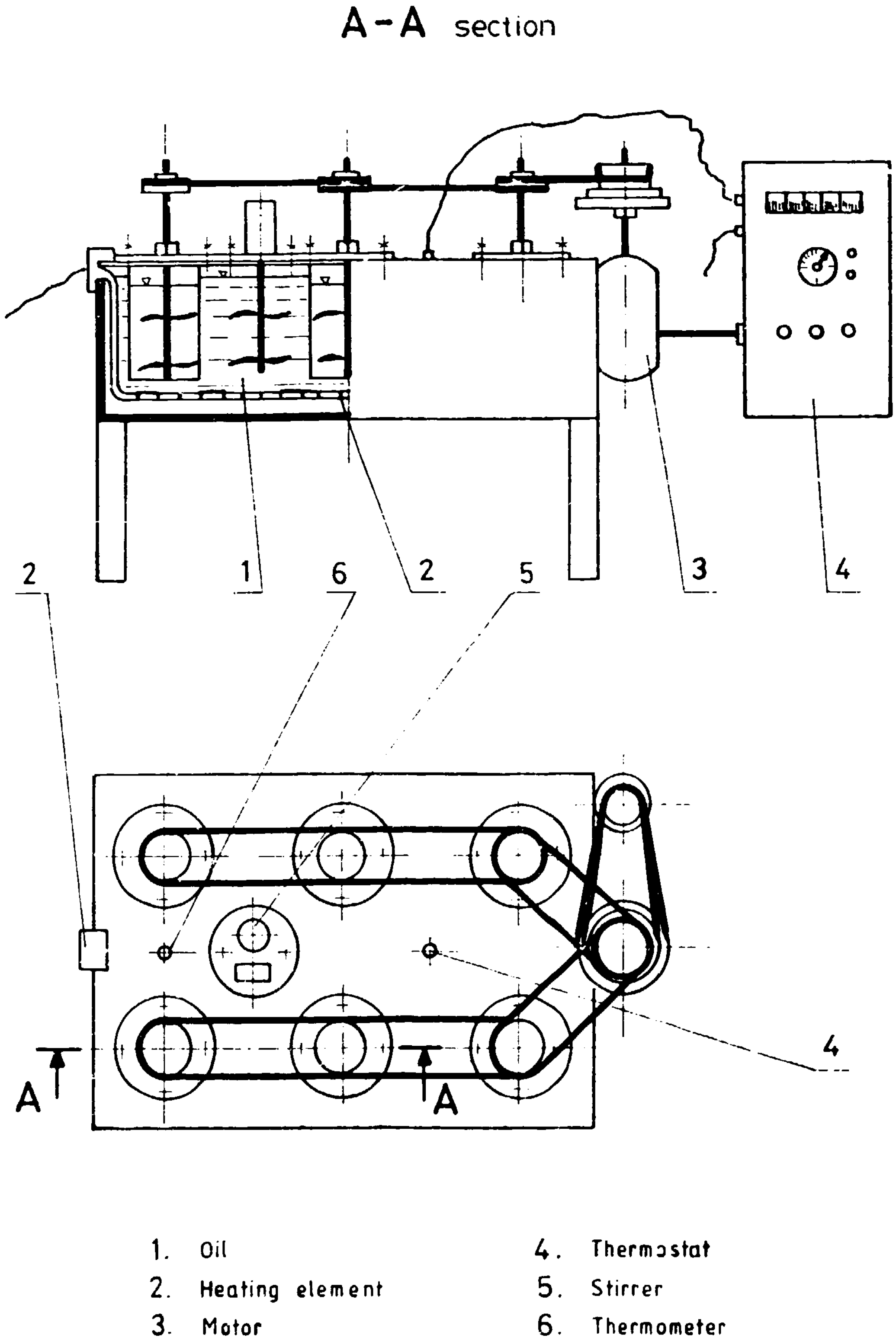

Fig.22. Mechanical laboratory precipitator

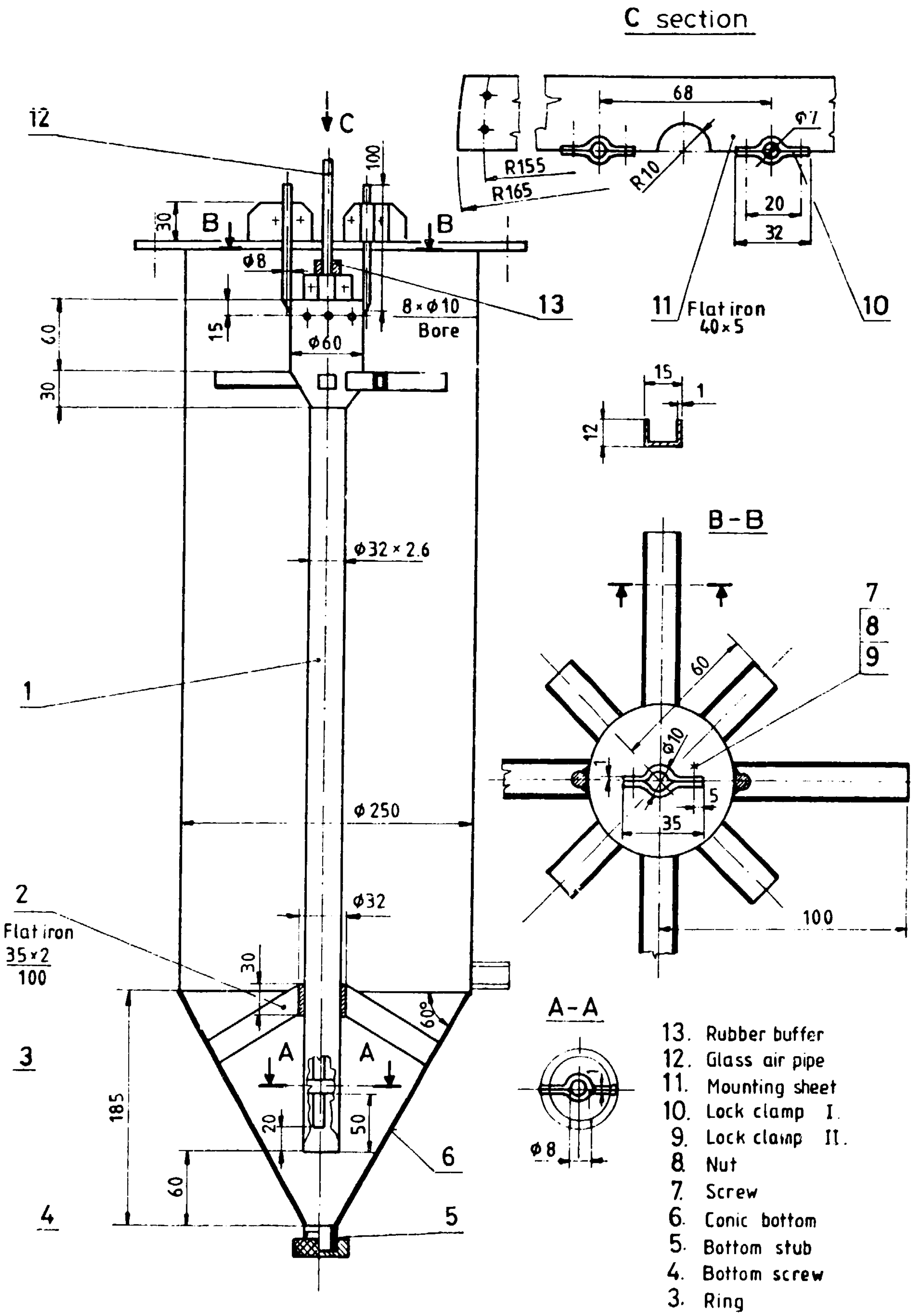

Fig.23. Laboratory air-precipitator tank

13. Rubber buffer
12. Glass air pipe
11. Mounting sheet
10. Lock clamp I.
9. Lock clamp II.
8. Nut
7. Screw
6. Conic bottom
5. Bottom stub
4. Bottom screw
3. Ring
2. Outrigger
1. Airlift

washed, dried alumina hydrate /at 140°C in an autoclave/ and by diluting it. In some cases for studies of impurity effects synthetic sodium aluminate solution is used, which can be prepared by dissolving calculated quantity of aluminium chips in pure NaOH solution and by diluting it to the desired concentration. Adding various impurities to the solution their influence on precipitation can be studied.

PROCEDURE

Make sure that the bottles are preheated to the initial temperature of precipitation.

Pour 1 liter of sodium aluminate solution of appropriate concentration and molar ratio into each bottle.

Cover the precipitator in order to avoid evaporation. Wait for thermal equilibrium.

Calculate the seed quantity as described in PRINCIPLES and weigh seed on a technical balance and add it to the preheated sodium aluminate solution. Start stirring and heating cycle.

Determine precipitation efficiency using the following data of previous experiments:

/i/ initial concentrations of the solution:

90 g/l Na_2O_c
110 g/l Na_2O_c
130 g/l Na_2O_c
140 g/l Na_2O_c

/ii/ initial Na_2O/Al_2O_3 molar ratio: 1.6,
/iii/ seed ratio: 2.0,
/iv/ precipitation cycle: 50 hours,
/v/ initial temperature: 60°C,
/vi/ cooling rate: 0.2°C/h according to a linear program,
/vii/ adsorbed moisture of seed: 13 %,
/viii/ sampling: after 1, 2, 3, 4, 6, 12, 24, 30, 50 hours,
/ix/ plot the precipitation efficiency versus time and compare the curves for various concentration.

Note: Precipitation test is very lengthy hence laboratory practice can only cover starting the experiments and evaluating data of earlier tests.

14. CAUSTIZATION

PRINCIPLES

The aim of this operation is to regenerate caustic soda. The largest amount of caustic soda is lost as Na-Al-hydrosilicate, called "chemically bound soda" forming in red mud. The second largest source of loss is carbonate formation.

Both types of losses can be reduced by the causticization of red mud, the separated soda salt and the liquors.

Causticization of red mud

A waste material of alumina plants, red mud, contains sodium-aluminium-hydrosilicate /in short: NAS/. Its amount, composition and crystal structure depend on the alumina-to-silica ratio of bauxite and on the parameters of the Bayer process, such as temperature, liquor concentration, liquor impurities, etc.

Its composition is generally described as

$$3/Na_2O.Al_2O_3.2SiO_2/.Na_2X$$

where

X - different anions, like AlO_2^-, CO_3^{2-}, SO_4^{2-}, Cl^- etc.

Generally, there are several types of NAS forming together, each with a different efficiency of causticization /Fig.24/.

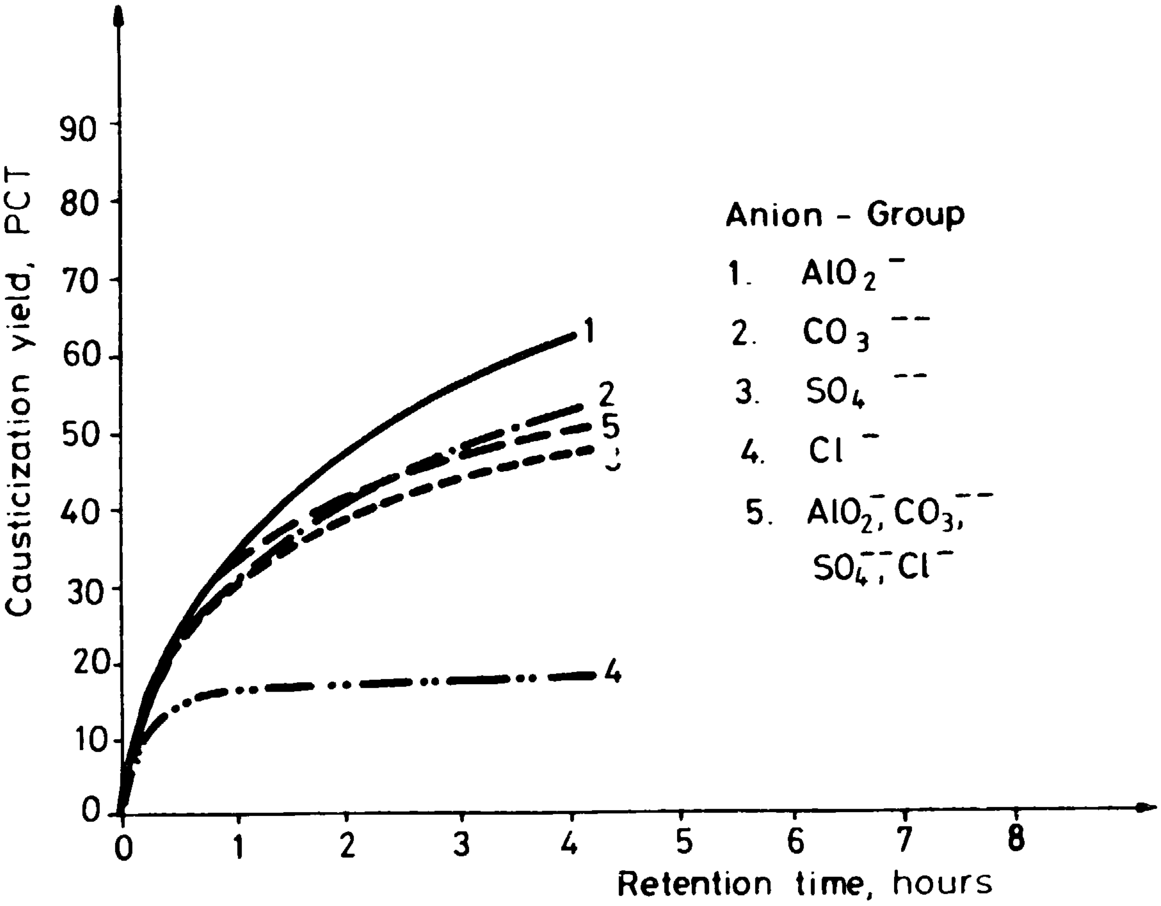

Fig. 24. Causticization curves of different Na-Al-silicates

The general equation of the causticization reaction:

$$NAS + Ca/OH/_2 \longrightarrow 3CaO.Al_2O_3.kSiO_2/6-2k/H_2O + NaOH$$

That is, calcium-aluminium-hydrosilicate /in short: CAS/ is formed to replace NAS, and the chemically bound soda dissolves as NaOH.

CAS is a hydro-garnet with a k value varying between 0.8 and 2.2. A well causticized red mud has a k value in the range of 1.6 - 1.8.

The efficiency of red mud causticization varies with the following parameters:

/i/ it rises with rising temperature,
/ii/ it saturates as a function of treatment time,
/iii/ it is proportional with the amount of lime until the $\frac{CaO}{Na_2O_{bond}}$ molar ratio of about 3, then it turns flat,
/iv/ it rises with decreasing initial solid concentration and
/v/ decreasing solid content of the starting slurry.

The influence of these parameters can be studied by laboratory experiments. Our laboratory program involves experiments concerning the influence of duration time and lime addition.

Causticization of soda

A potential source of serious technological deficiency, soda salt forms mainly from the carbonates of bauxite /calcite, dolomite, siderite/, to the detriment of caustic soda in the liquor.

The solubility of soda greatly depends on the concentration of the liquor and, to some extent of its impurities /P, V, F, C_{org}, etc/. Consequently, the allowable level of soda differs in different plants. The so-called American Bayer process, that involves diluted liquor, allows a soda level of 20-30 %. For plants working with European Bayer process, a level of only 12-14 % can be allowed without risking operational troubles and decreasing yields.

There are several ways to regenerate soda:

- the soda salt can be causticized after its separation from the liquor.
- the soda can be regenerated before digestion, adding lime to the bauxite slurry,
- and the soda can be regenerated from the liquor on the washing line.

The first way involves the separation and filtration of the salt, and these operations are tedious and expensive. The second way, also called "inside causticization" involves a very large specific consumption of lime and loss of alumina.

The third way, also called "outside causticization", is the one giving the best results. Therefore, we are going to deal with that one in detail.

The quality of lime /slaked or quick lime/ has a great importance in the soda causticization. Better results, that is, more effective utilization of lime and smaller alumina losses can be achieved by quick lime.

The outside causticization is based on three reactions:

slaking of the lime:

$$CaO + H_2O \longrightarrow Ca/OH/_2 + heat$$

reaction of calcium hydroxide with sodium carbonate:

$$Ca/OH/_2 + Na_2CO_3 \longrightarrow 2NaOH + CaCO_3$$

and with sodium aluminate, forming tri-calcium-aluminium-hidrate:

$$3Ca/OH/_2 + 2NaAlO_2 \longrightarrow 3CaO.Al_2O_3.xH_2O + 2NaOH.$$

The mechanism of the process is shown schematically in Fig.25.

The efficiency of soda causticization depends on the technological parameters the same way as that of red mud, see /i/ to /iv/.

The outside causticization yields a maximum amount of soda, if the amount of total soda is co-ordinated with the amount of soda in the form of carbonate /Fig.26/.

The optimum causticization results arise if

- a slow slaking lime is used,
- the temperature is kept at 95°C,

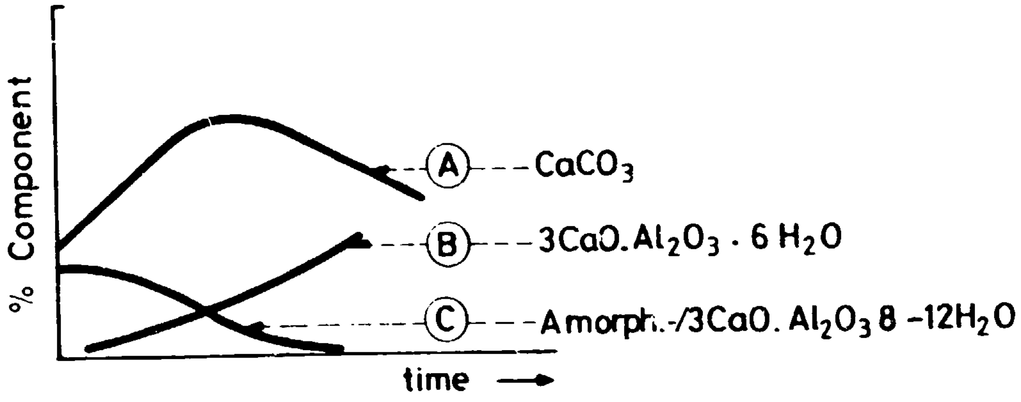

Fig.25. The reaction mechanism for quick lime causticization

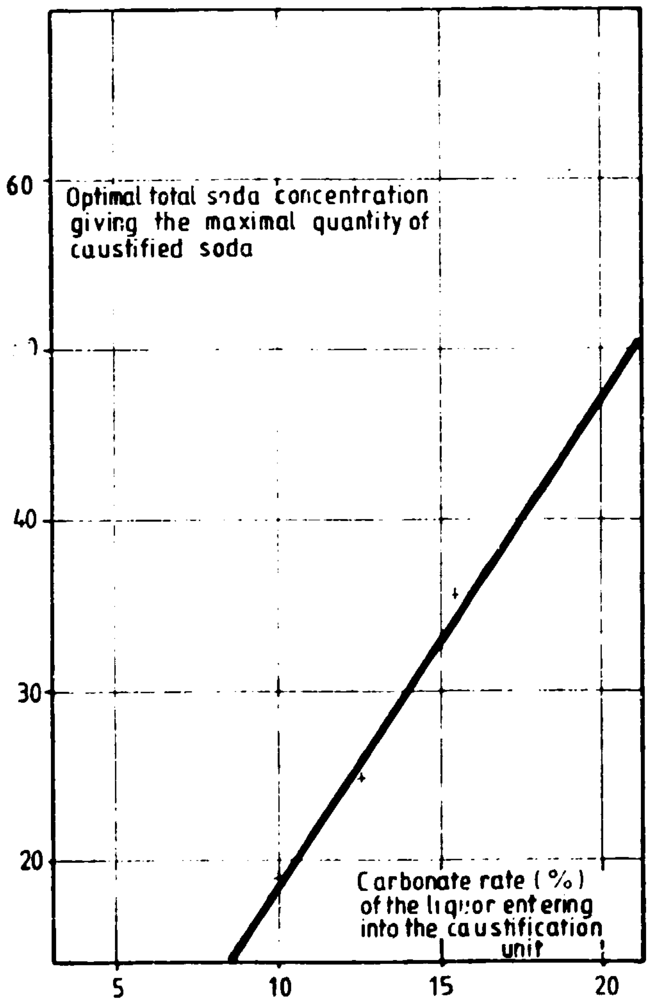

Fig.26. Caustification of overflowing liquor from washing muds

- the duration of the operation is above 120 minutes,
- the amount of lime added is sub-stoichiometric, /about 60-80 %/, depending on the concentration of the solution to be causticized.

EXPERIMENTAL

/i/ Causticization of red mud

Red mud from the last washing stage of the Almásfüzitő Alumina Plant is used for the experiments. The composition of both the liquid and solid phase are known.

The caustic soda content of the solution is equal to that of the overflow of the last washing stage: $Na_2O_{caust} = 5.7 \frac{g}{l}$,

$$\alpha_{caust} = \frac{Na_2O_{caust}}{Al_2O_3} = 2.19.$$

Materials and equipments

- Red mud, solid content: 1 kg,
- Diluted aluminate liquor, 3 l,
- 4 covered vessels, with stirrers, capacity: 1 liter,
- Thermostate accomodating several vessels.

/ii/ Causticization of soda

Liquor from the washing line of the Almásfüzitő Plant is used. The amounts of Na_2O_t, Na_2O_{cb}, and Na_2O_{caust}, that is, the total soda, soda in carbonate form and caustic soda are known.

Materials and equipments

- Quick lime, particle size: 300 micron, 1 kg,
- Diluted aluminate liquor, 3 l, $Na_2O_{caust} = 3.7 \frac{g}{l}$,

$$\alpha_{caust} = 2.19$$

- 4 covered vessels with stirrers, capacity: 1 liter,
- Thermostate accomodating several vessels.

PROCEDURE

/i/ Causticization of red mud

Experimental parameters:
temperature, T = 95°C,
duration, t = 4 hours,
solid content of the slurry: 250 $\frac{g}{l}$.

Pour 700 cm^3 of slurry containing 250 $\frac{g}{l}$ solids into each vessel. Add an amount of lime calculated by the formula

$$CaO = n \;.\; 0.7 \;.\; 2.5 \;.\; Na_2O_{bonded} . 56/62 \qquad /g/$$

where

n - amount of CaO /1, 2, 3, 4 moles/,

Na_2O_{bonded} - Na_2O, chemically bonded in the red mud
/Na_2O_{total} - $Na_2O_{adherent}$/. /%/

After adding the lime, cover the vessels and place them into the thermostate at 95°C and start stirring. Take a sample of 100 cm^3 hourly from one of the vessels, e.g. the one with 3 moles of CaO. Keep the other vessels closed till the end of the four hours´ time of treatment. Separate the slurries by means of a centrifuge to solid and liquid. Wash the red mud three times, repulping with 4-500 cm^3 of hot distilled water and centrifuge. Place the mud in an oven at 110°C to dry. Grind the mud to a grain size below 100 microns and have it analyzed by atomic absorption for Fe_2O_3, Al_2O_3, SiO_2, Na_2O, CaO, MgO, TiO_2 contents. Also have a determination of their loss on ignition made. Have the causticized liquors analyzed for their Na_2O_{total}, Na_2O_{caust}, Al_2O_3 and SiO_2 contents.

Evaluation

Calculate the efficiency of causticization as follows:

$$\eta_{caust} = \left(1 - \frac{a.b'}{a'.b}\right) . 100 \qquad /\%/$$

where:

a - Na_2O in causticized mud /%/,
a´ - Na_2O in original mud /%/,
b - Fe_2O_3 in causticized mud /%/,
b´ - Fe_2O_3 in original mud /%/.

Draw diagrams of the efficiency of red mud caustification as a function of

- lime addition,
- treatment time.

Use the following formula to calculate the number of moles of CaO allotted to 1 mole of regenerated Na_2O, for causticization with 1, 2, 3, 4 moles of CaO and 4 hours of duration:

$$n' = \frac{100.C}{a' \cdot \eta_{caust}} \cdot \frac{62}{56}$$

C - CaO in causticized red mud /%/,
a´ - Na_2O in the original red mud /%/.

/ii/ Causticization of soda

Experimental parameters:
temperature, T = 95°C,
duration, t = 2 hours.

Pour 750 cm^3 of liquor into each vessel. Add 25, 50, 75, 100 % of the stoichiometric amount of lime to regenerate the solution.

After adding the different amounts of lime to the vessels, cover and place them to the thermostate at 95°C, and start stirring.

When the two hours´ time of treatment is over, open the vessels and separate the slurries by means of a centrifuge. Discard the solid phases. Have all the liquors analyzed for their total soda, Na_2O_t, Na_2O_{cb} in carbonate form and caustic soda /Na_2O_{caust}/.

Evaluation

Calculate the theoretical demand of lime from the following formulae:

$$Na_2CO_3 + Ca/OH/_2 = CaCO_3 + 2NaOH, \text{ consequently:}$$

$$\text{theoretical } Ca/OH/_2 = 0.75.N_{cb}.\frac{74}{106}.n \quad /g/$$

where

N_{cb} - Na_2CO_3-content of the liquor /$\frac{g}{l}$/ .

0.75 - dilution factor,

74 - molecular mass of $Ca/OH/_2$,

106 - molecular mass of Na_2CO_3,

n - 0.25, 0.50, 0.75, 1.0: fractions of the theoretical amount of lime.

Convert the calculated amount of $Ca/OH/_2$ to the CaO basis, by the following formula:

$$CaO^{theoretical} = Ca/OH/_2^{theoretical} . \frac{56}{74} \; /g/$$

Calculate the efficiency of the causticization by the following formula:

$$\eta_{caust} = \frac{Na_2CO_3^f}{Na_2CO_3^{st}} \cdot 100 \quad /\%/$$

$Na_2CO_3^f$ - final soda content of the solution $/\frac{g}{l}/$,

$Na_2CO_3^{st}$ - soda content of the solution before treatment, "starting" soda content.

Draw a diagram of the efficiency of soda causticization as a function of the lime addition.

Knowing the caustic soda concentrations, the amount of regenerated sodium hydroxide can also be calculated for each lime addition. Calculate first the caustic soda increase, on the basis of the caustic soda concentrations in each solution, before and after treatment, by the following formula:

$$\Delta Na_2O_{caust} = 0.75/Na_2O^{final}_{caust} - Na_2O^{start.}_{caust}/ \quad /g/$$

$Na_2O^{final}_{caust}$ - final caustic soda content of the solution $/\frac{g}{l}/$,

$Na_2O^{start.}_{caust}$ - caustic soda content of the solution, before treatment, "starting" caustic soda.

Calculate the number of Na_2O moles /N/ formed at the addition of 1 mole of lime by the following formula:

$$N = \frac{/\Delta Na_2O_{caust}/_i}{62} \cdot \frac{56}{CaO_i^{theor}} \quad \text{mols of } Na_2O_{caust}$$

i - serial number of the lime addition and the caustic soda increase that belong together in the series of lime additions of 25, 50, 75 and 100 %.

Draw a diagram of the number of Na_2O moles yielded at the addition of 1 mole of lime, as a function of lime addition.

15. RED MUD SETTLING

PRINCIPLES

Industrial vs. laboratory settling

The most important parameter of the industrial settlers is specific loadability /kg/m^2 h/, the permissible solid mass flow through a horizontal cross section of unit area of the settler. Experimental determination of specific loadability, in plant scale is tedious and expensive. Consequently a laboratory scale investigation is needed for an estimation of the plant parameters. However, industrial settlers operate continuously, which is very difficult to imitate in the laboratory. Therefore, laboratory batch settling can only be a model of the industrial scale processes.

Modelling is based on the fact, that during gravitational settling, laminarity condition is fulfilled, i.e. settling velocity of solid particles /relative to the liquid/ is the same in both laboratory and industrial settlers, provided that parameters, like temperature, solid to liquid ratio, viscosity, etc. are the same.

The objective of laboratory scale investigation is to determine settling rate as a function of the solid concentration. The whole concentration range between the feeding and discharge /underflow/ concentration is of great importance.

A usual tube sedimentation experiment is carried out in a series of mm scale glass tubes filled with the prepared slurry of known solid concentration containing flocculant for speeding up settling. A settling diagram is derived by visual reading of the mud level as a function of time /H - t diagram/.

Types of settling diagrams

There are two main types of H - t diagrams, similar to curve 1 and 2 in Fig.27. Curve 1 shows a constant slope for shorter periods of time, later, reaching the so called critical point, the shape drops quickly. Curve 2 describes slurry with monotonously decreasing top velocity.

Theory of settling and the flux diagram

As a good approximation, local settling rate in the suspension is dependent only on the local solid concentration. Consequently, the solid flux, that is, the product of the solid concentration and the settling rate, also depends on the solid concentration only:

$$S = S/c/ = c \cdot u$$

where

S - is the solid flux of batch settling, /kg/m^2h/,

u - is the settling rate /m/h/, of the solid particles,

c - local solid concentration /kg/m^3/.

According to the experimental results, settling rate in real suspensions decreases with increasing the solid concentration.

Consequently, the dominant factor in the product of c and u is the increase of c in the low solid concentration range, and the decrease of u at higher concentrations. Therefore, the curve of batch settling flux vs. concentration starts steep at the origo, turns flat, then decreases monotonously through an inflexion point similar to Fig.28.

The flux diagram of a suspension fully characterizes settling and thickening. Solid concentrations corresponding to the maximum and inflexion points as well as the height of the maximum strongly depends on the characteristics of the mud and of the liquor. The type and dose of the added flocculant has importance, too.

Fig.28. gives the explanation of the sharp interface of the mud and the supernatant /i.e. the transparent liquor/ on the top of the slurry, as well for the thickening process inside the suspension.

Imagine the settling of an originally homogeneous slurry, corresponding to point A on Fig.28. Furthermore, suppose that the solid particles in the top mud layer have different settling velocities. Consequently, a bit later, the top mud layer has lower solid concentration then that below it. Thus, flux and solid concentration in the upper layer correspond to a point on the curve located left to A. The vector drawn from the origo to this point is steeper, that is, settling velocity is higher than that in the layers below. So the particles left behind catch up with the others. Consequently, the solid concentration and settling rate for all particles in the interface layer will be the same and the interface remains sharp. That results in a step like concentration variation /from c_A to zero/ at the top of

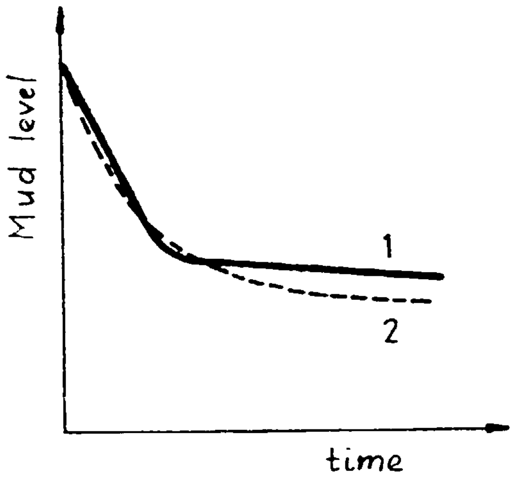

Fig.27. Settling diagrams

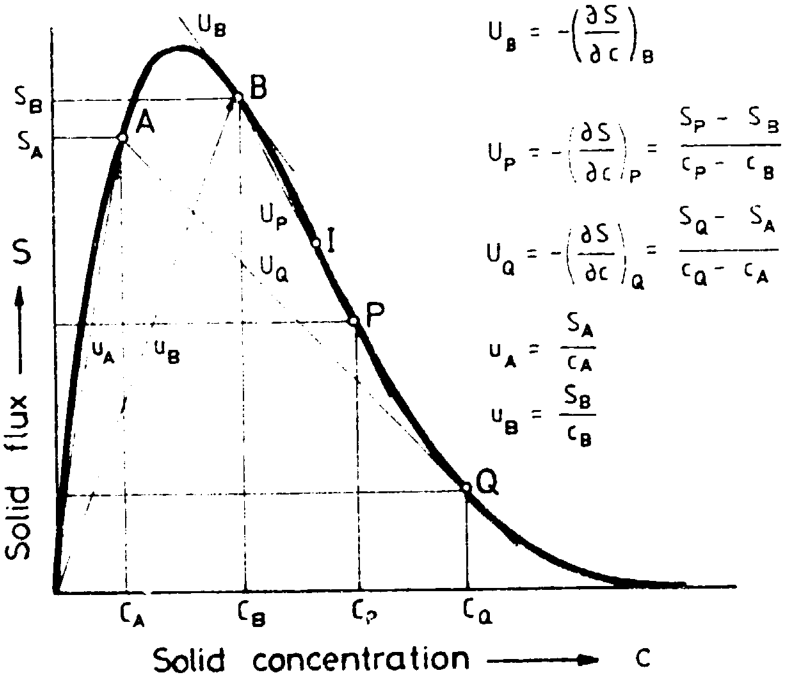

Fig.28. Typical batch settling flux diagram

the mud. Layers of solid concentrations between zero and c_A do not exist in the interface layer. The discontinuity migrates downwards by a velocity of U_A /see Fig.28/.

Thickening of the slurry, i.e. increase in the solid concentration causes an upward flow of the liquid. Any solid concentration state higher than the initial /homogeneous/ slurry concentration moves upwards from the bottom of the slurry column, as a consequence of the increase of solid concentration at the bottom.

Slope of the position vectors drawn to point S/c/ on the flux curve gives the settling velocity /u/ of the solid particles, migration velocity /U/ of a layer of solid concentration c is given by the slope of the tangent of the flux curve at concentration c. Concentration states with upward migration velocities lower than that of the layers behind, are "swallowed" by faster states. Therefore a discontinuity, similar to the one at the supernatant-mud interface can come about inside the slurry. The possible concentrations inside the slurry are determined by the maximum layer velocity.

The initial concentration state directly thickens at the bottom to solid concentration which is determined by this maximum velocity, i.e. by the maximum slope secant i.e. the tangent of the flux curve drawn from the initial concentration point. Consequently, the mentioned discontinuity always occurs in cases, in which the initial concentration is lower than that corresponding to the inflexion point of the flux curve. Otherwise thickening is continuous in the whole volume of the slurry.

Laboratory determination of the solid concentration profiles

Flux diagrams can be derived from solid concentration, profiles recorded at different times during settling. The best method for the determination of solid profiles of red mud slurries is based on the absorption of soft gamma rays. The method is illustrated in Fig.29. Similar to other absorption methods, the attenuation of the radiation is measured as a function of height and time. The transmitted intensity of the radiation is given by

$$I = I_1 \, . \, \exp/-a.c/$$

where

I_1 - the transmitted intensity, through the tube filled with clear supernatant liquor,

c - the solid concentration,/ kg/m^3/,

a - radiation attenuation coefficient, /m^3/kg/, depending on the attenuation coefficient and of the density both of the solid and of the liquid phase of the slurry. It is constant for a given red mud suspension.

Concentration profiles, so obtained for red mud slurries are of three main types as seen in Fig.30., dependent on the dose of flocculant.

Derivation of the flux diagram

The settling velocity, u_c, of the solid particles, in a layer of solid concentration c, can be determined from a

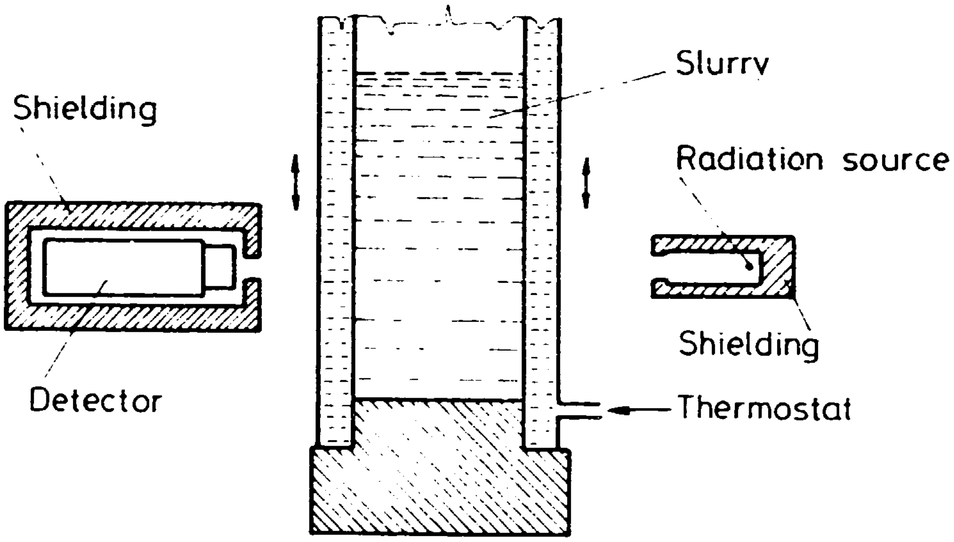

Fig.29. Fundamental scheme of the radiation absorption settling investigation

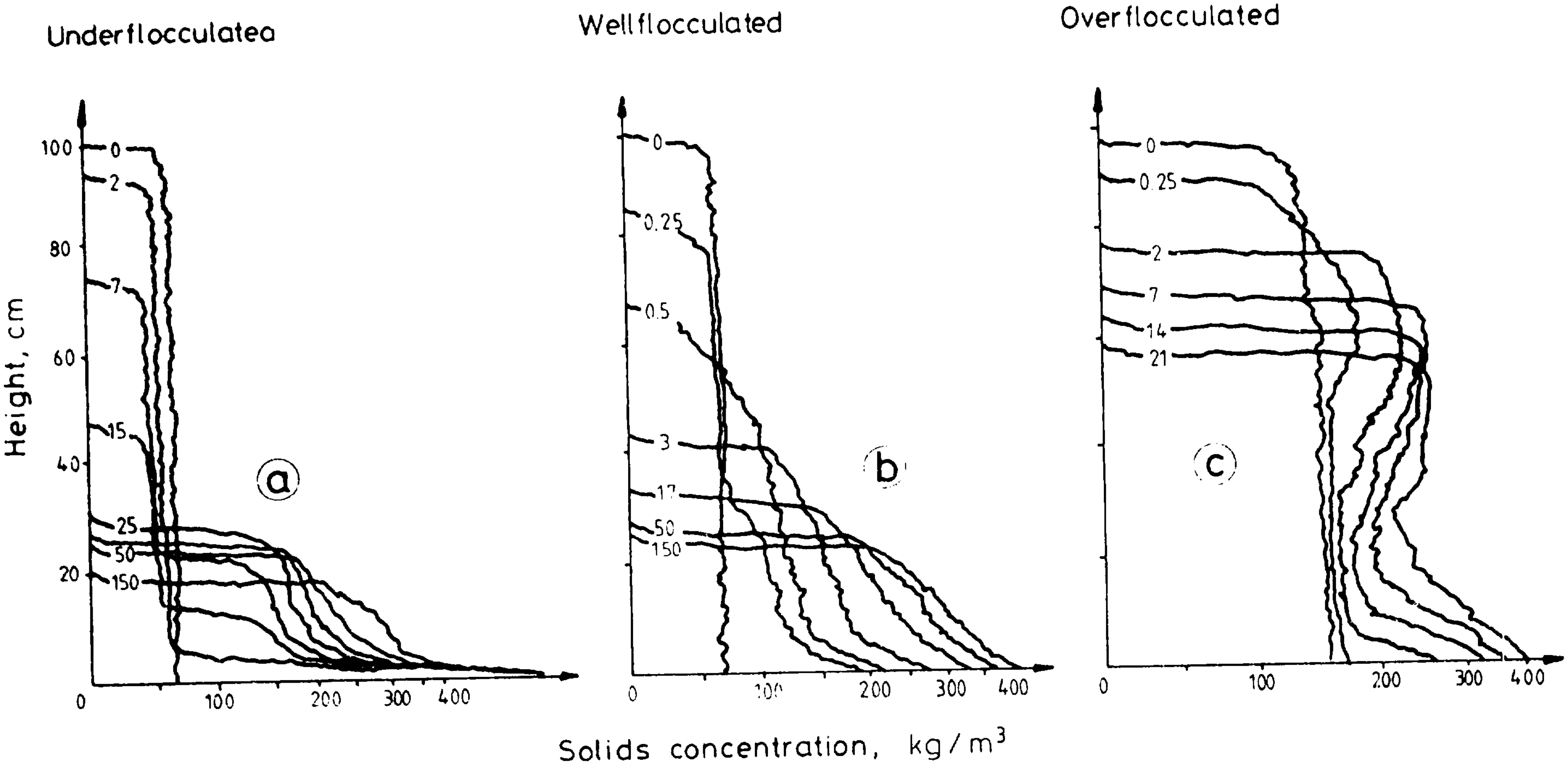

Fig.30. Significant solid profiles

series of concentration profiles. Fig.31. shows a detail of the series, taken at time t and t+ t, respectively. The vertical line drawn at solid concentration c crosses the profiles at heights z_c and $/z+\Delta z/_c$. The layer of concentration c migrates upward with a velocity of

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

The total mass of solid particles passing through this layer during Δt with a settling rate of u_c is:

$$m = /U_c + u_c/.c.\Delta t$$

referred to unit cross sectional area.

However, this value is equal to the sum of striped area, T, and the rectangular area, $c.\Delta z$, in Fig.31. Thus

$$/U_c + u_c/.c = c . \frac{z}{t} + \frac{T}{t}$$

Combining the tree equations, we get the solid flux:

$$S = u_c . c = \frac{T}{\Delta t}$$

The result can be made more accurate if we calculate average value for all the pairs at the same concentration.

Plotting the flux values as a function of the solid concentration we get the flux diagram.

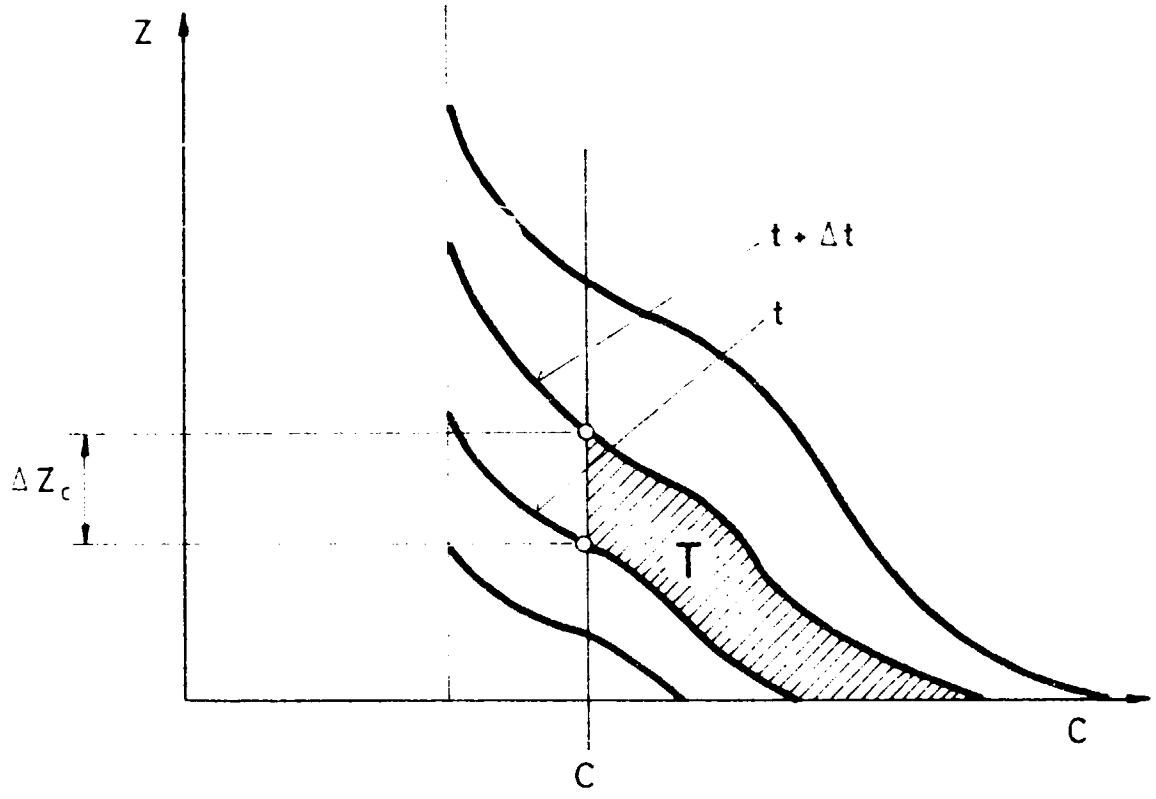

Fig.31. Calculation of the solids flux

Derivation of the settling velocity

The settling velocity of the particles passing through the layer of solid concentration c is of S_c/c.

The simple model of Stokes describing the movement of a single sphere of diameter D has to be corrected taking the influence of the solid concentration into account /Richardson - Zaki equation/:

$$u_c = u_o./1-c/\rho_s/^n$$

where

u_o - is the Stokes velocity,
ρ_s - is the density of the solid /g cm^{-3}/,
n - is an empirical constant depending on the Reynolds number.

This equation holds for ideal /nonflocculated, nonsolvated/ suspensions.

Taking the solvated floc structure of the red mud suspensions into account, the Michelson-Bolger formula applies:

$$u_c = u_o./1 - k.c/^{4.65}$$

where k is the volume of flocs produced by unit weight of dry solid.

Let us introduce the solvation factor α, as a measure of immobilized liquor bound in the focs:

$$\alpha = \frac{V}{v}$$

where

V - is the average volume of a floc,

v - is the volume of solid particles in the floc,

hence

$$k.c = \alpha.c/\rho_s$$

For ideal suspensions $\alpha = 1$.

Writing the Michelson-Bolger formula into

$$u_c^{1/4.65} = u_0^{1/4.65} \; . \; /1 - \alpha \frac{c}{\rho_s}/$$

it can be seen, that in a suitable chosen coordinate system we get a linear c dependence.

The settling-rate diagram in Fig.32., derived the way described above, shows two linear parts for a red mud suspension.

Stokes velocities can be derived from both intercepts /with the ordinata/, shereas solvation factors.

From both linear sections, Stokes velocity and solvation factor, α, can be calculated. The former as the intercept with the ordinata, the latter from the condition $\alpha c^{*}/\rho_s = 1$, that is $\alpha = \rho_s/c^{*}$, where c^{*} is the intercept with the abscissa.

Floc diameter, D, can be derived from a modified Stokes formula:

$$D^2 = \frac{510\alpha . u_0 . \eta}{\rho_s - \rho_l}$$

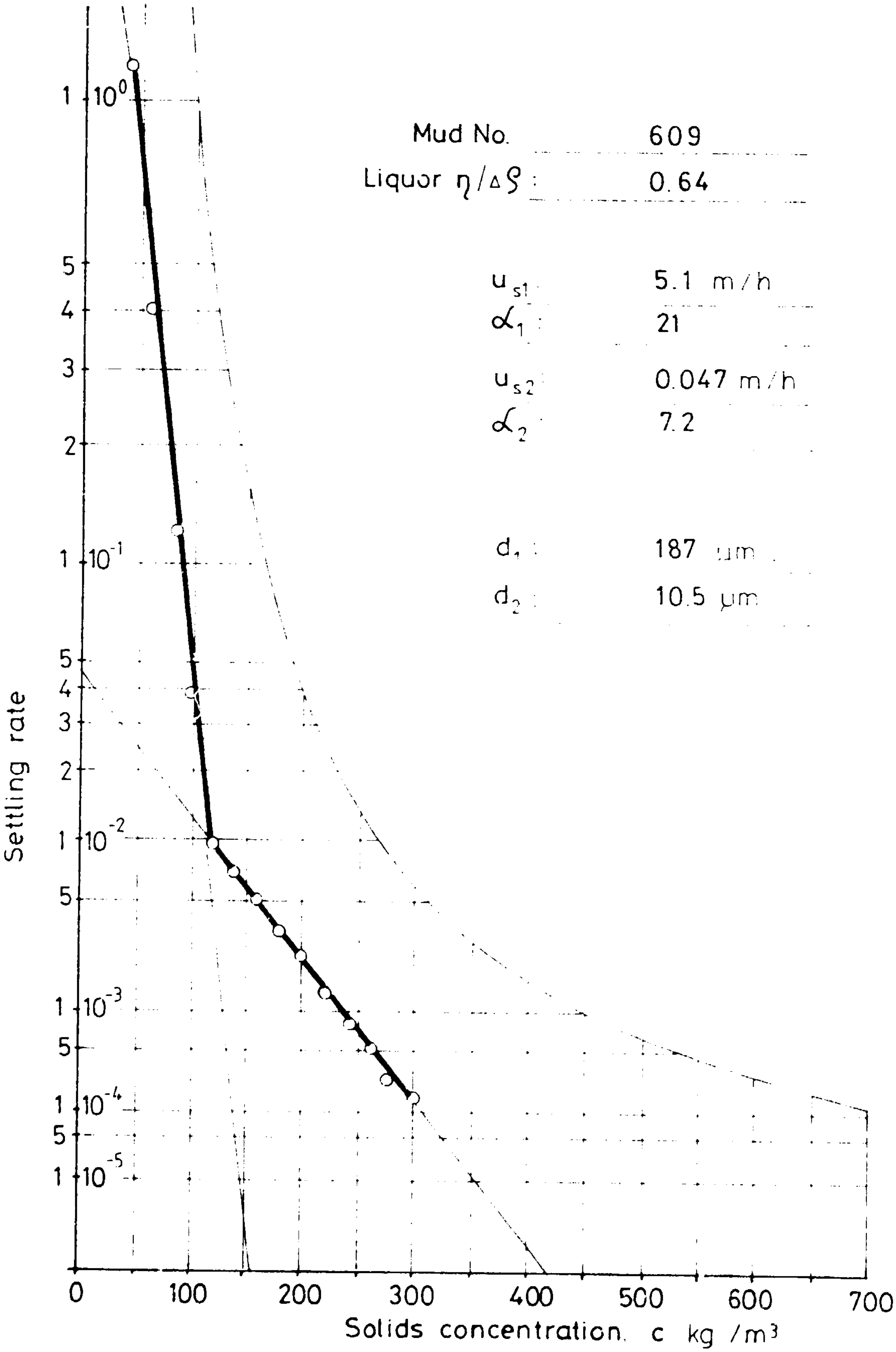

Fig.32. Settling rate diagram

for both sections. In the formula, ρ_s and ρ_l are the densities of the solid and liquid phases, respectively, and η is the viscosity of the liquor.

EXPERIMENTAL

The instrument used for laboratory settling experiment is a Soft-gamma-ray Absorption Model-settler /SAM/, developed and manufactured by ALUTERV-FKI, Budapest, is illustrated in Fig.29.

Settling of red mud suspension is observed in a double-wall temperature controlled sedimentation tube. The inside diameter of the tube is 6.5 cm, which is big enough for elimination of the wall-effect, and for sensitive measurement of the radiation absorption. By opposite sides of the settling tube a radiation source /18.8 GBq Am-241/ and a scintillation detector is mounted on a common elevator, which scans the whole length of the settling tube in preset time intervals.

The instrument operates automatically, plots the solid concentration profiles on an X-Y recorder, or collects data in the memory of a minicomputer. The initial solid concentration, $I/c_o/$, and the supernatant intensity, I_1, can be read off the X-Y plot, while c_o has to be determined by separating the mud in a centrifuge.

3.6 l of appropriately prepared red mud slurry is used in a model settling experiment on SAM.

Time intervals between consecutive measurements of concentration profiles should be determined by estimation from the results of previous measurements. Profiles should be taken more frequently at the beginning of the experiment then less and less frequently as settling slows down.

PROCEDURE

Prepare slurry from bauxite according to the procedures described in chapters 11 and 12 of this volume.

Prepare flocculant solution by boiling calculated quantity of flour in 50 ml of distilled water /or the way prescribed by the manufacturer if you use synthetic flocculant/.

Mix the flocculant solution with the slurry.

Pour the slurry /cooled to 90 deg C/ into the sedimentation tube of controlled temperature.

Start taking concentration profiles by SAM /demonstration/.

Evaluate results of previous experiments

> Draw H-t diagram by reading mud levels off the profile curves. Determine the initial settling rate of the mud level.
>
> Put the vertical positions of layers of constant solid concentrations onto the H-t diagram. Determine the upward migration velocity of those concentrations.

Using the computer printed data, plot batch flux diagram and settling velocity diagram.

Determine the characteristic floc parameters u_0, D and α from both linear sections of the velocity diagram.

16. PHYSICAL PROPERTIES OF ALUMINA

PRINCIPLES

When alumina trihydrate is calcined, water is eliminated, porosity is created, and eventually, if the temperature is pushed high enough, the porosity disappears and alpha-alumina is formed. The porosity which exists between temperatures of calcination of approximately 300° and 1100°C, at which alpha is formed, gives a large surface area which can adsorb water and/or other gases. It is the existence of surface area in the pores which is the basis of the dry scrubbing process which is now the accepted way to assure clean effluent from the smelting process.

While we can recognize that the term "degree of calcination" does not have a scientific basis, it is a useful concept for both the producer and the user of alumina. The producer is concerned about measuring degree of calcination because it is usually the way in which he ensures process control in the calcination process. For the purchaser of alumina, degree of calcination is a way of determining how much water he is buying along with his alumina. For the smelter man, degree of calcination helps define how much water is present, which affects his ore factor. It is a way to estimate properties which may affect his process efficiencies in the Hall-Héroult cell and more recently to predict the operating efficiency of the dry scrubbing process. A measure of degree of calcination which is meaningful to both producer and user will facilitate communication.

Most of the concern of both the producer and the user has been focused on the average property expressed as a specific measurement of the degree of calcination. As with any other average property, one must be aware of the spread of the property which this average represents.

Average properties of alumina

These average properties have also often no scientific meaning, they give one or two numbers as a result of prescribed - sometimes standardized - procedures.

Average properties of alumina can be classified into three groups:

physical parameters, like apparent and bulk density, angle of repose, grain size distribution, and others,

adsorption parameters, like benzene number, loss on ignition, LOI, and DLOI /LOI measured on water-saturated samples/, specific surface area, and others,

crystallographic parameters, like α/γ -Al_2O_3 ratio, absolute α-Al_2O_3 content, distribution refractive index of individual grains, etc.

However, literature often refers all of them as physical properties of alumina. These properties show tendencies of correlation. For sample, specific surface area decreases, density increases with increasing α-Al_2O_3 content.

Angle of repose and apparent density, however, do not show any correlation to the α-Al_2O_3 content. Aluminas can be classified also by properties relating to the size, shape and surface of the individual grains. Alumina of fine grains /floury alumina/ is adhesive, its angle of repose, benzene number, and apparent density is higher than those of the coarser /sandy/ alumina.

Non-uniformity of alumina

Depending on the mineralogical composition of the bauxite and the consequent diversity of the technological conditions of the Bayer process, the resultant alumina may show pronounced non-uniformity.

Taking only the calcination process into account, during industrial calcination, there will be a considerable variation in the time/temperature combination seen by individual particles. In rotary kilns, the degree of mixing, short-circuiting throught the traveling bed, and elution from the bed by the gas flow will determine the time/temperature region which each particle undergoes.

As an illustration of the influence of some calcination parameters, Fig.33. shows a comparision of correlation between specific surface area and α-alumina content for laboratory /Fig.33.a/ and industrially calcined /Fig.33.b/ aluminas. Spread of properties of individual alumina particles can be determined by measuring refractive index distribution under the microscope.

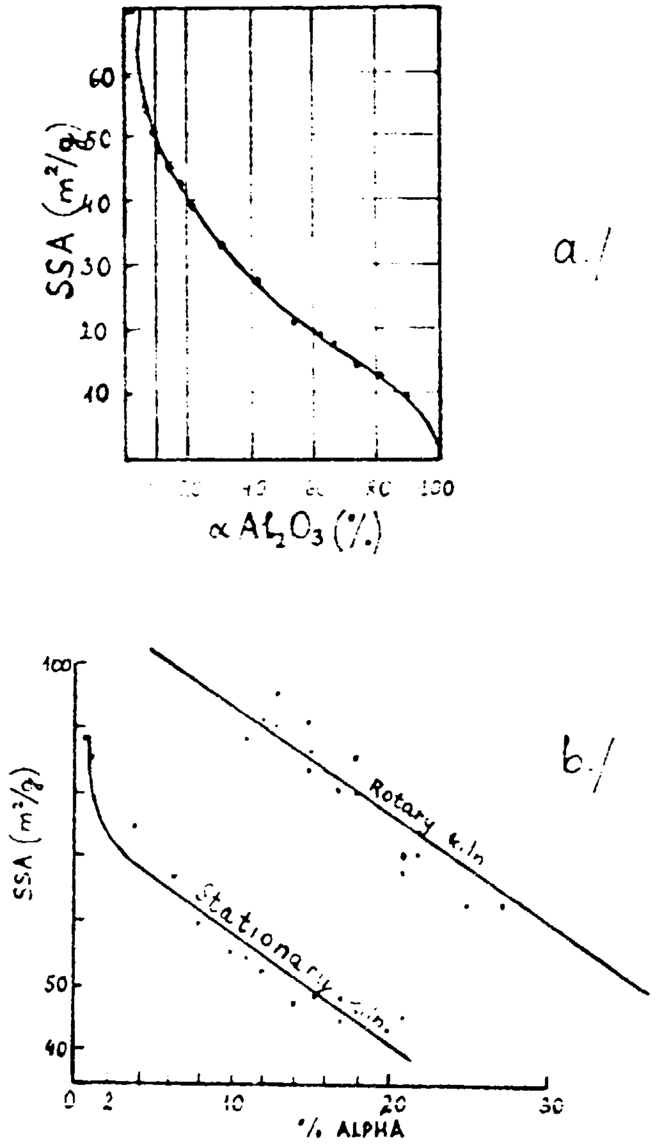

Fig.33. Relationship between specific surface area and percentage alpha-alumina for alumina calcined
a./ laboratory,
b./ industrially.

Fig.34. compares the refractive index distribution for aluminas from two different types of calcination kilns.

Temperature of digestion, molar ratio and other Bayer-parameters have also a great importance, concerning the physical properties of the resultant alumina.

Differences in correlation curves come about because the one-number average property is composed of different spreads of properties.

Floury vs sandy alumina

Based on the physical properties, two fundamental types of alumina may be distinguished:

- floury alumina, principally produced in Europe and fed to Söderberg-type cells,

- sandy alumina produced in plants applying American technology, and processed in cells with prebaked anodes.

Floury alumina is a poorly flowing powder containing an amount of fine, feathery crystals, together with larger spherical particles, which originate from the hydrate. These particles frequently show pronounced fragility resulting from hindered recrystallization, but sometimes they are obviously grains of Al_2O_3. Sandy alumina is a fairly uniform, relatively coarse, freely flowing powder, with a particle size distribution closely resembling to that of the original hydrate. This type of alumina often

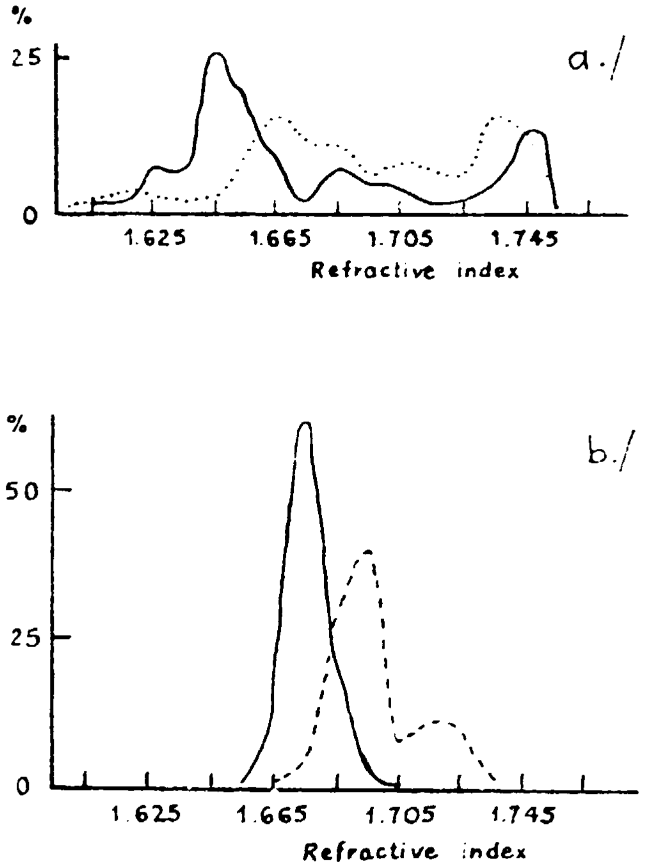

Fig.34. Refractive index distribution for alumina calcined
a./ in rotary kilns,
b./ in stacionary kilns.

contains grains of an undercalcined phase, α-Al_2O_3, which is opaque and shows affinity for dye-stuffs.

The most significant physical properties characterizing these two types of alumina are as listed in Table 11.

Table 11. The most important physical properties of floury and sandy aluminas

Physical property	Floury alumina	Sandy alumina
Loss on ignition	0.3 %	0.9-1.2 %
Specific surface area	5-10 m^2/g	40-45 m^2/g
Alpha alumina content	60-70 %	20-30 %
Specific surface area /m^2/g/	less than 10	more than 35
Apparent density	0.95-1 t/m^3	0.88 t/m^3
Angle of repose	40-45°	28-32°
Grain size > 100 mesh	0.1 %	2-8 %
Grain size < 325 mesh	50-55 %	6-10 %

The objective of this practice is to give a survey of some methods which serve as grading the alumina. Out of these, measurement of apparent density, angle of repose and α-Al_2O_3 content /by crystal-optical method/ will be discussed in detail.

A recent method, based on nuclear magnetic resonance /NMR/ will also be illustrated here, which, due to its speed can prove useful in process control.

Specific surface area measurements, X-ray diffraction determination of α-Al_2O_3 is covered in other chapters of this volume.

In the following, principles and experimental details of the methods will be discussed.

Determination of alumina phase composition by crystal-optical method

PRINCIPLE

Refraction index of alumina hydrate, transition and α-alumina is different. Phase transformations of alumina hydrate during calcination are followed by an increase in refraction index. A method developed for the determination of α-Al_2O_3 content, based on this phenomenon, can easily be carried out with a good reproduction.

This simple method is especially useful when /expensive/ X-ray diffractometric determination of α-Al_2O_3 content is not available.

When a crystal of unknown refraction index is immersed in a reference liquid of known refraction index, a contour line, the so called Becke line appears and moves towards the material of higher refraction index on raising the ocular of the microscope.

The explanation of this phenomenon is shown in Fig.35.

The refraction index of α-Al_2O_3 is between 1.752 and 1.768. The most suitable reference liquid is methylene-iodide /n = 1.74/, because of its appropriate refraction index and its relative stability . Phases of a refraction

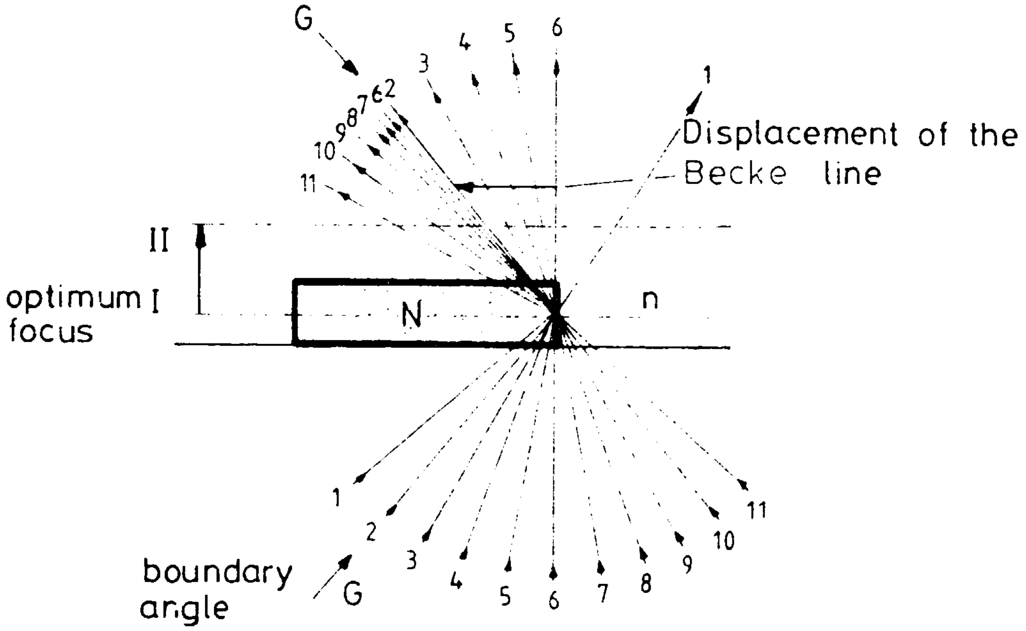

Fig.35. Explanation of Becke´s method

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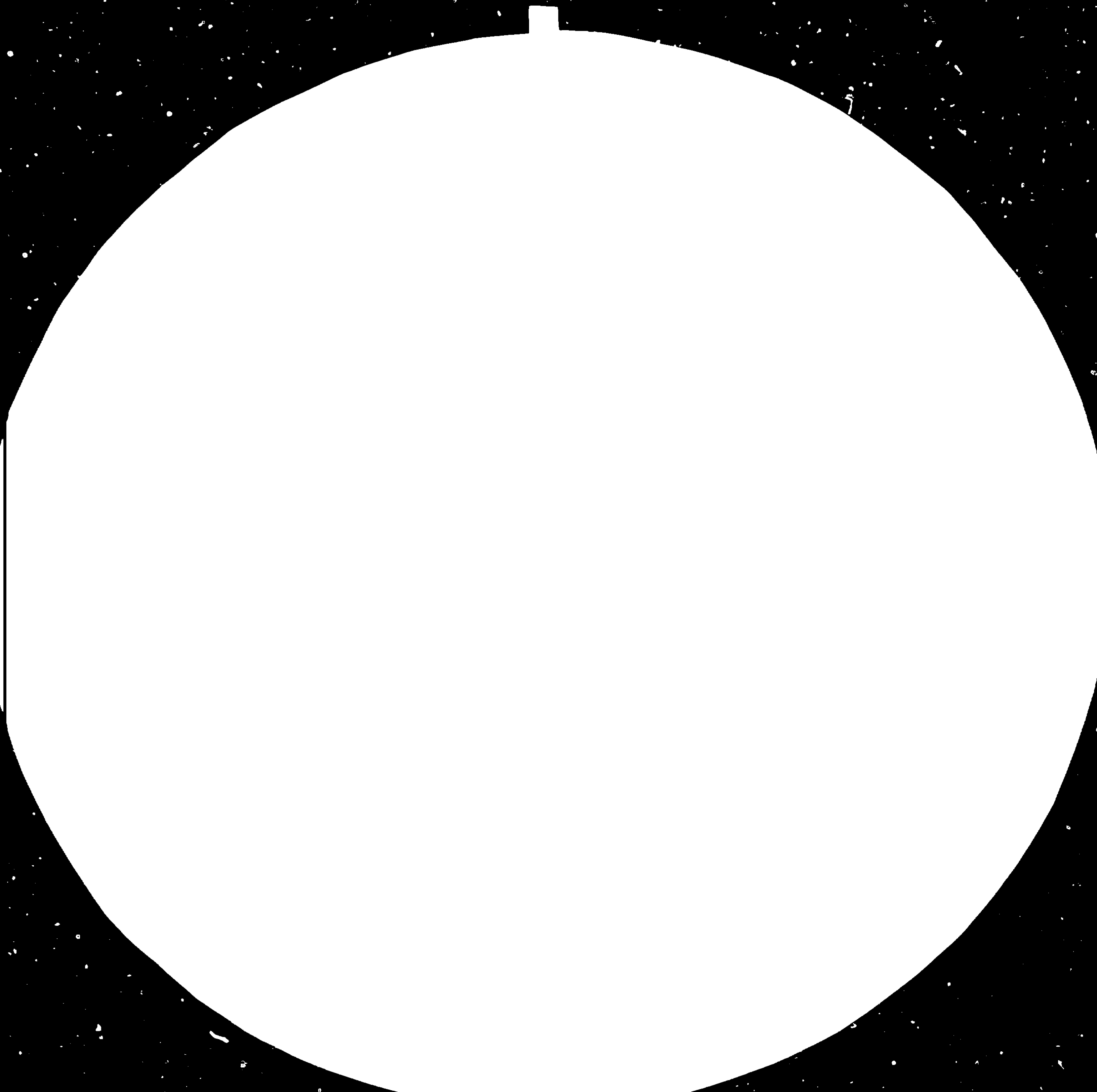

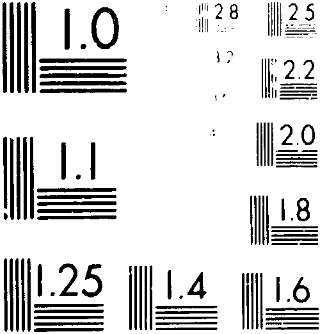

MICROCOPY RESOLUTION TEST CHART

[illegible]

index higher than 1.74 are called α-alumina. The other phases are classified as γ-alumina.
The contour of α-Al_2O_3 grains is light blue; raising the ocular, the Becke line moves inwards the grain. /Fraction I/.
Transition aluminas of lower refraction index have a negative contour and their colour is yellow-brown. /Fraction II/.

Concentration of different alumina phases is determined by counting alumina particles of different crystal-optical properties.

EXPERIMENTAL

Equipment and accessories

Transmission optical microscope,
Counting equipment,
Methylene-iodide, of refraction index 1.740,
Glass cover sheet.

Evaluation

Keyboard equipment is used for counting. The ratio of the two fractions can adequately be calculated only after counting at least 1.000 points. If the number of grains in fraction I. is A and that of fraction II. is B the percentage of α-alumina is calculated by

$$X_I = \frac{A.100}{A+B} \ \%$$

the percentage of "non-α" - say γ-alumina is:

$$X_{II} = /100 - X_I/, \ \%$$

PROCEDURE

Cone and quarter the sample down to 0.3 g. Sweep a little amount of alumina on the object carrier glass using a small brush, put it the cover sheet and drop a little methylene-iodide by the side of the sample. By moving the sheets, help the grains to distribute uniformly and to enter the liquid.

Fix the prepared sample under the objective lens and use magnification of 300/600 X. Use the ocular micrometer for counting the particles of different phases.

Determine the number of grains of fractions I. and II. by counting the spots, taking only those grains into account which are on crossing lines.

Compare results with results of X-ray diffractometry /available from the instructor/.

Determination of angle of repose

PRINCIPLE

Rough, air-dried alumina is allowed to flow through a funnel of definite size from a given height, without shaking, to a horizontal sheet and the foot angle of the formed cone is measured.

Equipment

The equipment consists of the following parts:

Funnel, made of stainless steel, supplied with a metal sieve,

Base-sheet, made of stainless steel or marble, polished surface, fixed horizontally, marked with two mm-scaled lines intersecting each other under the center of the funnel,

Funnel-holder, made of stainless steel fixed to the base-sheet,

Height adjusting cylinder.

PROCEDURE

Adjust the base line horizontal. Fit the height adjusting cylinder to the center pin of the base-sheet and screw the funnel into the holder. Remove the cylinder and put it aside.

Pour the air-dry, untreated alumina sample, into the middle of the funnel from a height of about 40 mm. Carry on the feeding until the top of the alumina cone reaches the funnel. A frustum cone will be formed which has a 6 mm diameter upper sheet.

Mark the foot of the alumina cone round, read the length of the 4 diameters of the cone.

Repeat the procedure 3 times, make note of the results.

Evaluation

Calculate the angle of repose /R/ in degrees by

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

where

H - height of alumina cone: the distance between the base sheet and the end of funnel stem /mm/,

D - mean of the 4 diameters /mm/,

d - inside diameter of the funnel stem /mm/.

Determination of apparent density

PRINCIPLE

Air-dry, raw alumina is allowed to fall into a cylinder of a known volume, standing on a firm horizontal base. The mass of alumina is divided by the volume of the cylinder /calibrated with water and expressed in gms/. The result is accepted as apparent density. Although the measurement is very simple, it should be performed very carefully.

EXPERIMENTAL

Equipment

Feeding funnel, made of glass.

Cylinder, made of glass, capacity: 200 ccm volume, height-diameter ratio: about 6 to 1.

Driving shell, made of glass.

Adjustable holder ring, mounted to a stand for fixing the feeding funnel.

PROCEDURE

Measurement of the volume /water value/ of the cylinder. Weigh the mass of the empty vessel, pour distilled water to the brim and weigh. The difference of the two values is the water value.

Determine the mass of a known volume of alumina. Mount the feeding funnel with the adjustable holder to the fixed stand so that the stem of the funnel have the same shaft as the cylinder, and the distance between the edge of the cylinder and the stem of the funnel be 10.0 cm. Place the driving shell on the edge of the cylinder so that it is close to the stem of the funnel, but does not touch it. Let the air-dry, raw alumina sample flow into the middle of the funnel from a height of 4 cm with a constant flow, taking care not to shake the equipment meanwhile.

Stop feeding alumina when the cone formed by the falling alumina rises above the edge of the cylinder. Remove the alumina excess above the cylinder volume lifting the funnel with the adjustable holder ring and pulling the driving shell lightly, pass the cylinder without moving it.

Clean the outer side of the cylinder and weigh it.

Evaluation

The apparent density /L/ is determined as the ratio of the mass of alumina and that water of the same volume.

Nuclear magnetic resonance determination of water in aluminas

Nuclei behave as minute moving magnets. If we put the specimen in external magnetic field axes of nuclei in the specimen orient in fixed directions with relation to the applied field. These directions correspond to discrete energy levels. Transitions between these levels are caused by the application of an oscillating magnetic field /the sample is placed inside a coil/.
The amplitude of the resonance signal is proportional to the number of the particular nuclei in the sample. Other parameters of the signal /width, etc/ are characteristic of the environment of the nuclei.

EXPERIMENTAL

The NMR equipment, simplified for water determination is manufactured by KFKI, Budapest. It consists of a temperature controlled permanent magnet and a complete NMR spectrometer. The derivative absorption amplitude is detected and displayed in percents /calibration is necessary, using a standard of known water content/.

PROCEDURE

Weigh 2 g of aluminas in each of 8 sample tubes. Measure water content as described in the user's manual.
Compare results with specific surface areas of the samples /data available/.