The Quantitative X-Ray Analysis of Bauxite. I. The System Hydrargillite-Boehmite-Goehtite-Haematite

A. Bezjak, T. Friš-Gaćeša, V. Uzelac, and I. Arapović

Institute of Light Metals, Zagreb, Croatia, Yugoslavia

Received December 6, 1961

A photographic X-Ray method for quantitative analysis of the main four-component system in bauxites is described. The required standard straight lines are given. The use of the overlapping haematite-goehtite line (d = 2.69 Å and d = 2.67 Å resp.) is shown theoretically to be possible and is experimentally verified.

INTRODUCTION

Bauxite is a mixture of minerals. Its aluminium component may occur in the form of mono- and trihydroxides. In the former case it is the mineral boehmite (γ -AlOOH) or diaspore (α -AlOOH), while the trihydroxide is known as hydrargillite (γ -Al(OH)₂). Iron is contained in the mineral goehtite (α -FeOOH) (called limonite if excess of water is present), or in haematite (α -Fe₂O₃). In most cases silicon is bound in the aluminosilicate kaolinite (2 SiO₂ · Al₂O₃ · 2H₂O), while titanium is in anatase (TiO₂).

Generally speaking the extraction of alumina from bauxites depends on its mineralogical composition. The well known Bayer process, for instance, cannot be efficiently applied to diasporic bauxites. If a bauxite contains predominantly boehmite it is processed under more severe conditions (the European Bayer process) than in the case of hydrargillite (the American Bayer process).¹

However, let aside other aspects of the Bayer process, the extraction procedure is not always related in a simple manner to the mineralogical composition of the raw material. Some investigations with Yougoslav bauxites led to the conclusion that the bauxite genesis plays an important role, but many questions remained unanswered.^{2,3,4,5} Further knowledge about the mineralogical composition of these bauxites is needed as the first step towards a more comprehensive solution of this problem.

The quantitative mineralogical analysis of bauxites has been done in the past in different ways. There are chemical methods for the two-component system hydrargillite-boehmite. In the indirect one^{6,7} the chemical analysis of a bauxite is used to calculate its mineral composition under cetrain assumptions, which makes it uncertain for precise work. The direct method³ makes use of the complete and partial extraction (in a strong alkaline solution) of hydrargillite and boehmite respectively. From the chemical analysis of the bauxite and the red mud after digestion one calculates the ratio hydrargillite/boehmite. The method is time-consuming and unsuitable for analysing a large number of samples.

The first quantitative X-Ray analysis of the mineralogical composition of bauxite components was published by Tertian and coworkers⁸. They also

studied the system hydrargillite-boehmite by relating the intensity ratio to the ratio of the concentrations, and calibration data are given. However, CuK radiation was used so that we could not apply these results for a system containing iron.

R. Black published simultaneousely his very interesting paper⁹. He investigated the dependence of the background intensity on the characteristic diffraction line intensities of all bauxite components (hydrargillite, boehmite, haematite, goehtite, kaolinite, quartz and anatase) for different concentration ranges. The author worked out diagrams from which one can read directly the content of a component by knowing the background and the line intensity. In this way the problem is completely solved, but we could not use the method because of lack of appropriate equipment. The method is also adapted for the American type of bauxites.

Ginsberg and Wefers¹⁰ looked into the possibility of applying the internal standard method. They used NaCl and $CaCO_3$, and an equipment with a counter. Natural and synthetized aluminium hydroxides were used. The authors conclude that the X-Ray analyses depends on the bauxite genesis i. e. on the crystallite size.

Rohner¹¹ applied Tertian's method to the system boehmite-diaspore and obtained satisfactory results.

In the present paper a photographic X-Ray method for quantitative mineralogical analysis of bauxites is described. The most frequently occurring components in Yugoslav bauxites are taken into account and the four-component system hydrargillite-boehmite-goehtite-haematite is first studied.

THEORETICAL CONSIDERATIONS

In this theoretical treatment of the problem the following symbols will be used:

G — hydrargilite (gibbsite)

B — boehmite

L — goehtite (limonite)

H — haematite

 $\mathbf{x}_{\mathbf{k}}$ — the concentration of the component $\mathbf{K} = \mathbf{G}, \mathbf{B}, \mathbf{L}, \mathbf{H}$.

 $HL_{2.68}$ — the total intensity of the 2.69 Å haematite and 2.67 Å goehtite lines.

d — the interplanar spacing.

$$\boldsymbol{x}_{\kappa}^{d} = \frac{\mathbf{k}_{G}^{u} \cdot \boldsymbol{\rho}_{\kappa}}{\mathbf{k}_{\kappa}^{d} \cdot \boldsymbol{\rho}_{G}}$$

$$\beta_{\kappa}^{d} = \frac{\alpha_{\kappa}^{d}}{\alpha_{B}^{d}}$$

the linear coefficient in equation (1) for the case of hydrargillite as the standard component.¹²

the linear coefficient in equation (1) for the case of hydrargillite as the standard component.¹²

 e_{G} the density of the pure component e_{K} (K = B, L, H.)

 $\begin{array}{l} k_K \\ k_G \end{array} \label{eq:kg} \mbox{the constants dependent on both the experimental conditions and the characteristic line intensity (with K = B, L, H.) \end{array}$

Bezjak¹² treated the concentration of one component as a function of the intensities of all components. We apply here this general solution to the four-component system of hydrargillite-boehmite-goehtite-haematite with the purpose of using the results for the quantitative mineralogical analysis of bauxites in respect to their four main constituents. As the basic component of the system we choose hydrargillite. The interdependece between the concentration and the intensity is given, acording to Bezjak¹², in the following way:

$$X_{\kappa} = \frac{\alpha_{\kappa}^{d} \cdot \frac{K_{d}}{G_{4.83}}}{1 + \sum_{\kappa} \alpha_{\kappa}^{d} \frac{K_{d}}{G_{4.83}}}$$

The expressions α_{K}^{d} and $K_{d}/G_{4:83}$ in equation (1) are partial contributions depending on the intensity K_{d} and $G_{4:83}$ and on α_{K}^{d} as well. The partial contribution of the basic component is one. Hence,

$$X_{G} = \frac{1}{1 + \sum_{K} \propto_{K}^{d} \frac{K_{d}}{G_{4,83}}}$$
(2)

It is concluded from (1) that one has to determine α_d^K for each component i.e. for boehmite, goehtite and haematite. The concentration, intensity and α_K^d are connected through

$$\frac{X_{\kappa}}{X_{G}} = \alpha_{\kappa}^{d} \cdot \frac{K_{d}}{G_{4.83}} \qquad (\text{see ref. 12.}) \qquad (3)$$

Therefore, in order to determine a_{K}^{d} we measured the dependence of $K_{d}/G_{4,83}$ on the known concentration ratios x_{B}/x_{G} , x_{L}/x_{G} and x_{H}/x_{G} . According to equation (3) the results should be straight lines whose slopes are $1/a_{K}^{d}$.

(1)

In case there is no hydrargillite in the sample one can transform the coefficients $\alpha_{\mathbf{K}}^{d}$ using boehmite as the basic component. The new coefficients are $\beta_{\mathbf{B}}^{d} = \alpha_{\mathbf{K}}^{d}/\alpha_{\mathbf{B}}^{d}$ and equation (1) becomes

$$x_{\kappa} = \frac{\beta_{\kappa}^{d} \cdot \frac{K_{d}}{B_{6.23}}}{1 + \sum_{\kappa} \beta_{\kappa}^{d} \frac{K_{d}}{B_{6.23}}}$$

(4)

where K is now G, L, or H.

The equations (1) and (2) can be applied rigorously if the counting method is used, because in that case the absorption does not depend on the diffraction angle. However, if one uses the film method with a cylindrically shaped sample appreciable errors may arise due to absorption. No large differences in μ R of separate constituents or mixtures are encountered in bauxites. A calculation shows that in the most inconvenient case (pure aluminium related to pure iron components) the correction factor for the intensity ratio is 1.05. This factor is approximately constant and between unity and 1.05 for bauxite i.e. for mixtures. We therefore did not correct for absorption while using the preceding equations in the numerical evaluation of the results.

It will be shown later, that in course of this investigation it became necessary to make use also of the strongest 2.69 Å haematite line in spite of the fact that it almost coincides with the goehtite line at d = 2.67 Å. Such a course of attack is usually avoided, but the present theoretical considerations and the obtained results show not only that it is possible to use a combination line, but that in certain cases it yields more accurate results. The required transformation for this purpose of the basic equation (1) is as follows.

By means of the coefficients $\alpha_L^{2.69}$ the partial contributions in eq. (1) of haematite and goehtite are calculated for the four component system.

The partial contributions for goehtite and haematite in the denominator of eq. (1) are:

$$\boldsymbol{\varkappa}_{H}^{2.69} \frac{\mathsf{H}_{2.69}}{\mathsf{G}_{4.83}} + \boldsymbol{\varkappa}_{L}^{2.67} \frac{\mathsf{L}_{2.67}}{\mathsf{G}_{4.83}}$$
(5)

while in the numerator the haematite contribution is:

The mutual intensity $HL_{2.68}$ for the haematite line d = 2.69 Å and goehtite d = 2.67 Å is:

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$$\mathsf{HL}_{2.68} = \mathsf{H}_{2.69} + \mathsf{L}_{2.67} \tag{7}$$

In the same way we have

$$\alpha_{L}^{2.67} \cdot L_{2.67} = \alpha_{L}^{4.15} \cdot L_{4.15}$$
(8)

i.e.

$$L_{2.67} = \frac{\alpha_{L}^{4.15}}{\alpha_{L}^{2.67}} \cdot L_{4.15}$$
(9)

The partial contributions of haematite and goethtite in the denominator of eq. (1) are recalculated according to (5) and (7) as follows:

By introducing (9) into (10) one obtains:

$$\alpha_{\rm H}^{2.69} \frac{{\rm H}_{2.69}}{{\rm G}_{4.83}} + \alpha_{\rm L}^{2.67} \frac{{\rm L}_{2.67}}{{\rm G}_{4.83}} =$$

$$= \alpha_{\rm H}^{2.69} \frac{{\rm H}_{2.68}}{{\rm G}_{4.83}} + \left(\alpha_{\rm L}^{2.67} - \alpha_{\rm H}^{2.69} \right) \cdot \frac{\alpha_{\rm L}^{4.15}}{\alpha_{\rm L}^{2.67}} \cdot \frac{{\rm L}_{4.15}}{{\rm G}_{4.83}}$$

$$(11)$$

For the numerator it holds:

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On introducing the expressions (7) and (8) into the equation (1) one obtains the amount of haematite in the discussed four-component system:

$$X_{H} = \frac{\alpha_{H}^{2.69} \frac{HL_{2.68}}{G_{4.83}} - \alpha_{H}^{2.69} \frac{\alpha_{L}^{4.15}}{\alpha_{L}^{2.67}} \cdot \frac{L_{4.15}}{G_{4.83}}}{1 + \alpha_{B}^{6.23} \frac{B_{6.23}}{G_{4.83}} + \alpha_{H}^{2.69} \frac{HL_{2.68}}{G_{4.83}} + \left(\alpha_{L}^{2.67} - \alpha_{H}^{2.69}\right) \cdot \frac{\alpha_{L}^{4.15}}{\alpha_{L}^{2.67}} \cdot \frac{L_{4.15}}{G_{4.83}}}{\frac{L_{4.15}}{G_{4.83}}}$$
(13)

The last expression remains the same also for the other components except that in the numerator one puts

$$\alpha_{\rm B}^{6.23} \cdot B_{6.23}/G_{4.83}$$
 for $x_{\rm B}$ and $\alpha_{\rm L}^{4.15} \cdot L_{4.15}/G_{4.83}$ for $x_{\rm L}$.

The problem of using overlapping X-ray lines in order to determine quantitatively the haematite amount is therefore theoretically solved. The same procedure can be applied to other similar systems.

EXPERIMENTAL

The apparatus and the experimental conditions

The standard photographic method was applied using the Philips »Metalix« apparatus with the Debye camera of diameter 57.4 mm. The capillaries were of 0.3 mm diameter. CoKa radiation and an iron filter were used. Constant conditions for exposure and developing were maintaind within the experimental possibilities. »Ilford« Industrial X-Ray film was used through-out these measurements.

The intensity measurements were done on a Zeiss microphotometer. The mean value of the minimum background on both sides of a line was always subtracted from the maximum intensity of the corresponding line.

Sample preparation

Pure constituents (hydrargillite, boehmite, goehtite and haematite) were needed for the preparation of the standard mixtures.

The product obtained by the Bayer process is hydrargilite. We used a sample having a purity of $99.9^{9}/_{0}$ Al(OH)₃. The powder X-Ray photographs gave clear lines of hydrargillite.

Boehmite can be obtained in different ways (see for instance ref 13.). We tried the hydrolysis of amalgamated aluminium¹³. The product did not have sharp

X-Ray lines possibly due to very small crystallite size. The loss on ignition was also larger than the theoretical one, which suggests that some $Al(OH)_3$ gel was present too.



Fig. 1. The standard straight line for the system hydrargillite - boehmite (G_{4.83}, B_{6.23})

The method described by Torkar¹⁴ proved very satisfactory: pieces of 99.99 aluminium were heated in a hydrothermal bomb for 3 hours at 230°C.

The mineral goethite was obtained from the Mineralogical Institute of the Mining Faculty. It contained $96.0^{\circ}/_{0}$ goethite, the main admixtures being SiO₂ and MnO. The powder photographs showed clear lines of goethite.

Haematite was prepared by precipitating $Fe(OH)_3$ from a FeCl₃ solution. After subsequent heating at 900°C the product was $100^{\circ}/_{\circ}$ Fe₂O₃ with clear powder diagrams of haematite. For comparison natural haematite obtained from the same source as goehtite was also used.

Using the above described pure components, standard mixtures of different composition were prepared for the three two-component systems: hydrargillite-boehmite, hydrargillite_goehtite, and hydrargillite-haematite. Before the mixture



Fig. 2. The standard straight line for the system hydrargillite — goehtite ($G_{4.83}$, $L_{4.15}$) Fig. 3. The standard straight line for the system hydrargillite — goehtite ($G_{4.83}$, $L_{2.67}$)

preparation each sample was pulverized in an agate-mortar and subsequently passed through a sieve of 53 microns mesh size.

The homogenizing of the mixtures was done with a magnetic stirrer under acetone for 3 hours. Three independent mixtures were used to control their homogenity.



Fig. 4. The standard straight line for the system hydrargillite — haematite ($G_{4.83}$, $H_{3.67}$)



Fig. 5. The standard straight line for the system hydrargillite — haematite ($G_{4,83}$, $H_{2.69}$)

The mean value of the intensity ratio $K_d/G_{4.53}$ was used and the standard deviation calculated for each experimental point. The coefficients $\alpha_K^{\ d}$ were determined by the least squares mtehod

$$\alpha_{\kappa}^{d} = \frac{\left[\omega X X\right]}{\left[\omega X Y\right]}$$

where $X = x_K/G$, $Y = K_d/G_{4.83}$ and $\omega = 1/\sigma^2$.

The symbol [] means summing up over all experimental points. The standard straight-lines

The hydrargillite-boehmite system: the following characteristic lines were chosen according to Brindley¹⁵: d = 4.83 Å (10) for hydrargillite and d = 6.23 Å (10) for boehmite. The results are given in Fig. 1.

The hydrargillite-goehtite system: d=4.83 Å (10) for hydrargillite; d=4.15 Å (10) and d=2.67 Å (6) for goehtite. Fig. 2. shows the standard straight line, while in Fig. 3 are given the values calculated for the ratio $L_{2.67}/G_{4.83}$, which will be needed later.

The hydrargillite-haematite system: d = 4.83 Å (10) for hydrargillite; d = 3,67 Å (7) and d = 2.69 Å (10) for haematite. Because we had considerable difficulty with this system in the course of experiments, two sets of measurements, one with the artificial and the other with the natural haematite, were done. The results were the same within the experimental error and are represented together in Fig. 4. The values calculated for the case $G_{4.83}$ and $H_{2.69}$ are reproduced in Fig. 5.

The obtained coefficients for different diffraction lines of the standard mixtures are given in Table I.

\mathbf{K}_{d}	α_{K}^{a}	β_K^{a}			
$\begin{array}{c} {\rm G}_{4.83} \\ {\rm B}_{6.23} \\ {\rm L}_{4.15} \\ {\rm L}_{2.67} \\ {\rm H}_{3.67} \\ {\rm H}_{2.69} \end{array}$	1 0.98 1.31 2.51 1.91 0,71	1.06 1 1.34 2.57 1.95 0.73			

TABLE I

RESULTS

The quatitative X-Ray analysis was checked on several synthetic fourcomponent mixtures of different composition. The basic equation (1) requires that intensities of pure lines be used. The haematite line of strongest intensity is that for d = 2.69 Å (10), but it coincides with the goehtite line of d = 2.67 Å (6) if the small Debye-camera is used. We therefore used for haematite the free line at d = 3.67 Å (7).

The numerical evaluation of the results according to the equation (1) and $\alpha_{\rm K}{}^{\rm d}$ values from Table I. is as follows:

$$x_{6} = \frac{1}{1 + 0.98 \frac{B_{6.23}}{G_{4,83}} + 1.31 \frac{L_{4.15}}{G_{4.83}} + 1.91 \frac{H_{3.67}}{G_{4.83}}}$$
(14)



The results obtained are not quite satisfactory, the errors being sometimes larger than $\pm 5\%$ (see Table II.). After recalculating the results for the three-

TABLE II

No.	Component	taken in %	found in ⁰ / ₀	
1.	G B L H	$\begin{array}{c} 40.3 \\ 20.1 \\ 14.5 \\ 25.1 \end{array}$	39.4 22.8 13.2 24.6	0.9 + 2.7 1.3 0.5
2.	G B L H	49.5 24.9 11.8 13.8	44.6 23.7 12.8 18.9	$4.9 \\1.2 \\ + 1.0 \\ + 5.1$
3.		20.2 40,5 29.2 10.1	19.5 35.6 27.5 17.4	-0.7 -4.9 -1.7 +7.3

component system (hydrargillite-boehmite-goehtite) the error was substantially smaller, about $\pm 2^{\circ}/_{\circ}$. This suggested the use of the strongest haematite line at d = 2.69 Å (10) although it overlaps with the goehtite line at d = 2.67 Å. This resulted in theoretical considerations described earlier in this paper.

By putting the α_{K}^{d} values from Table I into eq. (13) one obtains the following expressions for calculating the concentrations of haematite, boehmite, hydrargillite and goehtite through the overlapping line HL_{2.68}:

$$X_{H} = \frac{0.71 \frac{HL_{268}}{G_{4.83}} - 0.37 \frac{L_{415}}{G_{4.83}}}{1 + 0.98 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.98 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.98 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.98 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.98 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.98 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}$$
(20)
$$X_{G} = \frac{1}{1 + 0.98 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.94 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.98 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.94 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.98 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.94 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.94 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.94 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.94 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.94 \frac{B_{6,23}}{G_{4.83}} + 0.71 \frac{HL_{268}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.94 \frac{B_{6,23}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.94 \frac{B_{6,23}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}}{1 + 0.94 \frac{B_{6,23}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.94 \frac{B_{6,23}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.94 \frac{B_{6,23}}{G_{4.83}} + 0.94 \frac{L_{415}}{G_{4.83}}}{1 + 0.94 \frac{B_{6,23}}{G_{4.83}} + 0.94 \frac{L_{4.83}}{G_{4.83}}}{1 + 0.94 \frac{B_{6,23}}{G_{4.83}} + 0.94 \frac{L_{4.83}}{G_{4.83}} + 0.94 \frac{L_{4.83}}{G_{4.83}} + 0.94 \frac{L_{4.83}}{G_{4.83}} + 0.94 \frac{L_{4.83}}{G_{4.83}} + 0.94 \frac{L_{4.83}}{G_{4.8$$

The concentrations in the synthetic mixtures were calculated according to the last set of equations through the overlapping line for goehtite and haematite and the results are given in Table III.

DISCUSSION

The results obtained with synthetic »bauxites« show that the quantitative ratios for hydrargillite-boehmite-goehtite-haematite are accurate to within $\pm 3^{0/0}$ absolute error, which is satisfactory for the film-method. The overlapping lines have not been used so far. It was considered that in such cases the total intensity cannot be used at all. The problems were therefore solved by using the free lines, which made considerable difficulties if these lines were of low intensity. We have shown here both theoretically and experimentally (for haematite) that such lines can be used and that more accurate results are obtained than by using weaker but free lines. This is particularly true for lower concentrations of haematite. For larger concentrations the film-method produces larger errors because of too strong intesities, which are difficult to

TABLE III					
No.	Component	taken in º/o	found in ⁰ /o		
1.	G B L H	40.3 20.1 14.5 25.1	39.6 23.6 13.2 24.2	-0.7 + 2.9 	
2.	G B L H	49.5 24.9 11.8 13.8	48.1 25.4 13.7 12.8	-1.4 + 0.5 + 1.9 - 1.0	
3.	G B L H	20.2 40.5 29.2 10.1	$21.2 \\ 38.4 \\ 29.7 \\ 10.7$	$+1.0 \\ -2.1 \\ +0.5 \\ +0.6$	

TABLE III

measure accurately. In such cases the relatively weak haematite line is strong enough for the quantitative determinations of haematite in a four-component system. The experimental data suggest that in the range of $5-20^{\circ}/_{\circ}$ haematite it is better to use the overlapping line at d = 2.63 Å, while above $20^{\circ}/_{\circ}$ the free line at d = 3.69 Å is preferred. The lower limit to the method is set by about $5^{\circ}/_{\circ}$ of each component.

Apart from the four basic components studied here bauxites contain SiO_2 usually bound in kaolinite, and TiO_2 as anatase. For a complete quantitative mineralogical analysis of bauxites one should make additional measurements for the system hydrargillite-kaolinite-anatase. In our preliminary measurements of this kind we experienced difficulties owing to the rather low content of kaolinite and anatase in bauxites.

The other direct way for putting the results on a bauxite basis is to make absolute measurements for at least one component by using an appropriate standard. The pertinent experiments are in progress and the results will be published in due course.

We therefore applied for the time being less direct methods of combining the chemical analysis data with those from the X-Ray measurements.

a) The Fe_2O_3 — basis.

The X-ray analysis yields the content of goehtite and haematite in the four-component system. By subtracting the corresponding amount of water from goehtite one obtaines the Fe_2O_3 content in the four-component system. The ratio of the Fe_2O_3 from the chemical analysis to that one from the X-ray data results in the following factor:

$$\mathrm{f}=~rac{\mathrm{Fe_2O_{3,\mathrm{chem}}}}{\mathrm{Fe_2O_{3,\mathrm{X}}}}$$

The final result on the bauxite basis is therefore obtained by multiplying the X-ray data with f, but the method is uncertain owing to the X-ray error and a relatively low content of Fe_2O_3 in bauxites.

b) The Al_2O_3 — basis.

The data on the Al₂O₃ - content from the chemical and the X-ray analysis can similarly be used. When the bauxite sample contains an appreciable amount of kaolinite which is visible on the X-ray photograph, then the corresponding amount of Al_2O_3 should, of course, be subtracted from the Al_2O_3 value of the chemical analysis. This method is better, because the Al₂O₃ amount is substantially larger than of Fe₂O₃, so that the X-ray error becomes less important.

c) The use of the total chemical analysis.

From the total chemical analysis one first subtracts the TiO₂ and kaolinite percentage (plus quartz if present which is estimated from the X-ray photograph). The recalculation factor is

$$f = \frac{100 - (0/0 \text{ TiO}_2 + 0/0 \text{ kaolinite})}{100}$$

In our applications of the X-ray analysis to natural bauxites we made use mainly of this last method. Some twenty samples from Herzegowina were analysed in this way. The results were quite satisfactory, the error being substantially less than 3% in comparison with the chemical analysis of the same samples. These results will be published in detail elsewhere.

Acknowledgment. We thank Professor D. Grdenić for making available to us the microphotometer in the Department of Structural and Inorganic Chemistry of the »Ruđer Bošković« Institute. Thanks are also offered to Professor M. Karšulin for enabling the synthesis of the boehmite samples in the Department of Physical Chemistry of the Technological faculty, and to Mineralogical Institute of Mining for the haematite and goehtite samples.

REFERENCES

- 1. R. S. Sherwin, J. Metals 2 (1950) 661.
- 2. S. Maričić, Kemija u industriji, 7 (1954) 201.
- 3. S. Maričić, I. Lugar, and T. Marin, Arhiv kem., 26 (1954) 133.
- 4. S. Maričić, I. Markovčić, and M. Vidan, Kemija u industriji, 5 (1957) 137.
- 5. E. Hermann and S. Maričić, Arhiv. kem. 26 (1954) 153.
- 6. S. Maričić, Tehnički pregled 5 (1953) 61.
- R. Podhorsky, Ibid. 6 (1954) 23.
- 7. A. Bezjak, E. Horvat, S. Maričić, and N. Rafaeli: »The mineral composition of the Novigrad and Drniš bauxites« (unpublished).
- 8. R. Tertian, R. Houssemaine, Ch. Legrad, and M. Tertian, Bull Soc. Chim. France 20 (1953) 423.
- 9. R. Black, Anal. Chem., 25 (1953) 5, 743. 10. H. Ginsberg, and K. Wefers, Erzmetalle, 10 (1957) 499.
- 11. F. Rohner, *Chimia* **12** (1958) 289. 12. A. Bezjak, *Croat. Chem. Acta* **33** (1961) 197
- 13. R. Fricke, K. Jockers, Z. anorg. Chem. 262 (1950).
- 14. K. Torkay, Mh. Chem. 91 (1960) 653.
- 15. G. W. Brindley, X-Ray Identification and Crystal Structures of Clay Minerals, The Mineralogical Society, London (1951) 265.

IZVOD

Kvantitativna rendgenska analiza boksita. 1. Sistem hidrargilit-bemit-getit-hematit

A. Bezjak, T. Friš-Gaćeša, V. Uzelac i I. Arapović

Razrađena je rendgenska metoda za kvantitativno određivanje osnovnih mineralnih komponenata hidrargilit — bemit — getit — hematit u boksitu. Izvršena su baždarna mjerenja za sisteme hidrargilit — bemit, hidrargilit — getit i hidrargilit — hematit. Kao karakteristične linije uzete su za hidrargilit d = 4,83 Å, za bemit d = 6,23 Å, za getit d = 4,15 Å, za hematit d = 3,67 Å i zajednička linija hematita i getita d = 2,68 Å. Teoretski je dokazana mogućnost upotrebe superponiranih intenziteta hematita i getita za kvantitativno određivanje hematita a ispitivanja na četverokomponentnim sistemima pokazala su da je za količinu od 5—20% hematita bolje upotrebiti zajedničku liniju hematita i getita d = 2,68 Å, dok je za veće količine hematita preko 20% prikladnije upotrebiti slobodnu liniju d = 3,67 Å. Opisanom metodom određuje se preko kemijske analize. Rađeno je standardnom fotografskom metodom. Upotrebljeno je CoKa zračenje i kamera $\phi = 57,3$ mm.

INSTITUT ZA LAKE METALE ZAGREB

Primljeno 6. prosinca 1961.