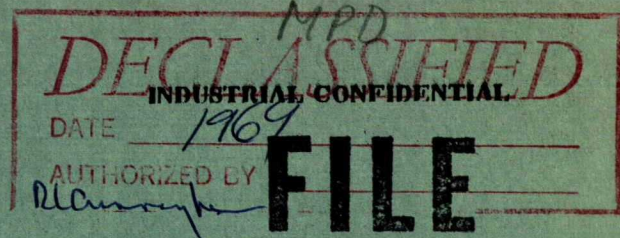


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CANADA



DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 66-2

**X-RAY DIFFRACTION INVESTIGATION OF
EIGHT BAYER PROCESS 'RED MUD' RESIDUES
FROM THE ALUMINUM COMPANY OF
CANADA, LIMITED, ARVIDA, P. Q.**

by

R. S. DEAN

MINERAL PROCESSING DIVISION

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SUMMARY OF RESULTS

The Guinier-deWolff 4-sample powder diffraction camera, used with a cobalt-target X-ray source, was able to detect 2 - 3% gibbsite in iron- and titanium-rich Bayer process 'red mud' residues.

The detection limit for boehmite appeared to be somewhat lower.

Other constituents identified within the 'red mud' samples were goethite, hematite, anatase, rutile, quartz, zircon, calcite and carbonate apatite. The detection of minor constituents (including the aluminium hydroxides) was facilitated by chemical removal of iron oxides. The partial segregation of constituents which occurred during high-speed centrifugation also proved to be useful for identification purposes.

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INTRODUCTION

On October 21, 1965, eight samples of 'red mud' alkali-insoluble (bauxite) residues from the Bayer Process plants of the Aluminum Company of Canada, Limited, Arvida, Quebec, were submitted to the Mineral Processing Division by Mr. J.S. Lobos, Chief Chemist.

The object of this investigation was to examine possible applications of the Guinier-deWolff 4 - sample X-ray powder diffraction camera (1) to the detection and estimation of aluminium hydroxides and various other constituents of the 'red muds'.

It was also requested that an attempt be made to resolve discrepancies which had become evident between determinations of gibbsite and boehmite by X-ray diffraction and chemical techniques.

PROCEDURE

Small portions of each of the eight samples under investigation were finely ground by hand in an agate mortar. Mounts for the Guinier-deWolff X-ray powder camera were prepared by packing 0.015 g portions of each ground sample into individual compartments of the standard 4 - specimen sample holders. The mounted powders were firmly pressed against a backing of "Scotch" brand No. 850 polyester tape by means of a rectangular plexi-glass tamping device, the end of which was covered by thin polyethene film in order to prevent powder adhesion. Powder patterns were obtained using cobalt X-radiation and an exposure time of 5 to 6 hours.

Preliminary examination of the resultant films indicated that sample No. 22758 was, mineralogically, the most complex, and hence a logical choice for use in phase concentration tests.

In the first of these tests, iron oxide removal by the method of Mehra and Jackson (2, p. 319) was followed by the NaOH differential dissolution treatment of Hashimoto and Jackson (3) and subsequently by leaching at room temperature with an excess of 2% acetic acid. However, Guinier X-ray powder photographs taken of the residue obtained following each of these treatments disclosed that hematite and goethite remained as prominent constituents of the treated material even though the red colour of the sample had completely disappeared. Examination of the residue revealed the presence of

many rounded, black, ferruginous grains, which appeared to have been only superficially attacked by the chemical treatment.

The iron oxide removal procedure was repeated on a one-gram portion of sample No. 22758 powder which had been ground for 60 minutes in a Fisher Automatic (agate) Mortar, and X-ray powder photographs prepared of the residue before and after further treatment with 2% acetic acid. Again it was found that iron oxide removal had been incomplete. Apparently, small aggregates had formed which prevented effective grinding of the ferruginous particles.

Effective comminution was finally accomplished by grinding two grams of the untreated powder in a Fisher Automatic Mortar, with methanol, for 80 minutes. The alcohol prevented any visible particle agglomeration. The suspension was then transferred into two 50 ml Nalgene centrifuge tubes and the solids collected by centrifugation for 10 minutes at 10,000 rpm in a Sorvall SS-3 Superspeed Centrifuge. Thirty millilitres of distilled water were added to each tube and the residues dispersed by magnetic stirring. The washed powder was dewatered by centrifugation, dispersed in a small (10 ml) volume of water, and then transferred to a 250 ml beaker. To this slurry the chemical ingredients for free iron oxide removal were added: 120 ml of 0.3 M sodium citrate solution, 30 ml of 1.0 M sodium bicarbonate solution, and finally, when the solution had been heated to approximately 80°C in a water bath, 3.0 g of solid sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$). A digestion period of 15 minutes was allowed, during which the solution was stirred intermittently. According to Mehra and Jackson (2, p. 319) these quantities of chemicals are capable of dissolving approximately 1.5 g of extractable Fe_2O_3 . Most of the red colour disappeared a few minutes after the solid sodium dithionite was added. The residue was recovered by centrifugation, washed, and the iron oxide removal treatment repeated with a digestion period of 45 minutes. Following this second treatment, no residual ferruginous grains were observed.

A Guinier-deWolff X-ray powder photograph was taken of the treated powder after it had been collected by centrifugation and washed twice with demineralized distilled water.

Centrifugation at 10,000 rpm resulted in segregation of a thin white layer at the top of the predominately grey iron oxide-free residue. Powder photographs were made of this white material before and after it had been boiled for 2 1/2 minutes in a stainless steel beaker containing 200 ml of 0.5N NaOH solution. This differential dissolution treatment was designed to remove gibbsite, allophane, and amorphous silica and alumina (3). Powder photographs were also taken of the grey material underlying the white layer before and after a similar NaOH treatment, and also of the NaOH-treated grey residue which had been stirred for 30 minutes in an excess of 2% acetic acid solution. In every instance, material being readied for irradiation was washed twice with demineralized distilled water prior to drying.

RESULTS

Guinier X-ray powder patterns of the eight original samples are illustrated in Figure 1 (No. 1 - 8), along with those of various mineral standards (No. 15 - 25). The relative abundance of their various constituents, as estimated from the overall intensity of the X-ray powder patterns, is given in Table 1.

Goethite was unique among the phases listed in Table 1 in that it yielded reflections which occurred invariably at slightly larger Bragg angles than those obtained from the standard material (pattern No. 16). Interplanar spacing measurements of the latter closely agreed with published X-ray data for goethite (4, p. 386).

A Nonius film-measuring scale was used for all interplanar spacing determinations made in the course of the present investigation. This device, which is calibrated according to the theoretical dispersion of the Guinier-deWolff camera (1° theta = 4mm), yields results which are sufficiently accurate for most routine identification purposes. Film expansion, the principal source of error in this method, is especially evident in contact prints such as those illustrated in Figure 1. For this reason, these are generally not suitable for interplanar spacing measurements, unless they have been individually calibrated with an internal standard.

In Table 2 the relative abundances of boehmite and gibbsite within the eight samples under investigation, as estimated from the Guinier X-ray powder data, are compared with the quantitative chemical and X-ray diffraction data obtained from the same samples by the Aluminum Company of Canada, Limited. The most obvious discrepancies occur in the case of sample C-39530 where the boehmite content has apparently been underestimated (especially by the X-ray method) and the gibbsite content chemically overestimated. Also, the chemical estimate of the gibbsite content of the Arvida 'Red Mud' - February 1963 sample appears to be high. A lower Guinier camera detection limit of roughly 2 - 3% gibbsite is suggested by these figures.

The chemical removal of iron oxides from Sample No. 22758 sharply enhanced the intensity of the reflections from all remaining constituents, including those from gibbsite and boehmite, as shown in Figure 1, pattern No. 9. The treated material also yielded reflections which could not be assigned to any of the constituents listed in Table 1. These reflections, including several which had formerly been masked by the iron oxide patterns, have been recorded in Table 3. Examination of these spacings indicated that the principal unknown phase within Sample No. 22758 was carbonate apatite. The X-ray powder data for this substance are shown in Table 3.

Figure 1 - Guinier-deWolff X-Ray Powder Diffraction Photographs

Cobalt radiation

Dispersion: 1° theta = 4 mm

Exposure Time: Nos. 1 - 15, 5 - 6 hours

Nos. 16 - 25, 2.5 hours

Pattern No.

- 1 No. 27154, Arvida Red Mud, February, 1963.
- 2 No. 27154, Arvida Red Mud, July, 1963
- 3 No. 27154, Arvida Red Mud, October, 1963
- 4 Synthetic Mud
- 5 No. 22757, Jamaica Mud
- 6 No. C-39530 ERM-265, Jamaica Mud
- 7 No. C-39778 JRM-365, Jamaica Mud
- 8 No. 22758, Jamaica Mud
- 9 No. 22758, iron oxides removed, (6.3 and 3.66A reflections from unidentified constituent are indicated)
- 10 No. 22758, iron oxides removed, 'white' fraction
- 11 No. 22758, iron oxides removed, 'white' fraction, after sodium hydroxide treatment
- 12 No. 22758, iron oxides removed, 'grey' fraction
- 13 No. 22758, iron oxides removed, 'grey' fraction, after sodium hydroxide treatment
- 14 No. 22758, iron oxides removed, 'grey' fraction after sodium hydroxide and acetic acid treatments.
- 15 Anatase
- 16 Goethite
- 17 Hematite
- 18 Boehmite
- 19 Gibbsite
- 20 Quartz
- 21 Calcite
- 22 Apatite
- 23 Rutile
- 24 Zircon
- 25 Kaolinite, with minor anatase

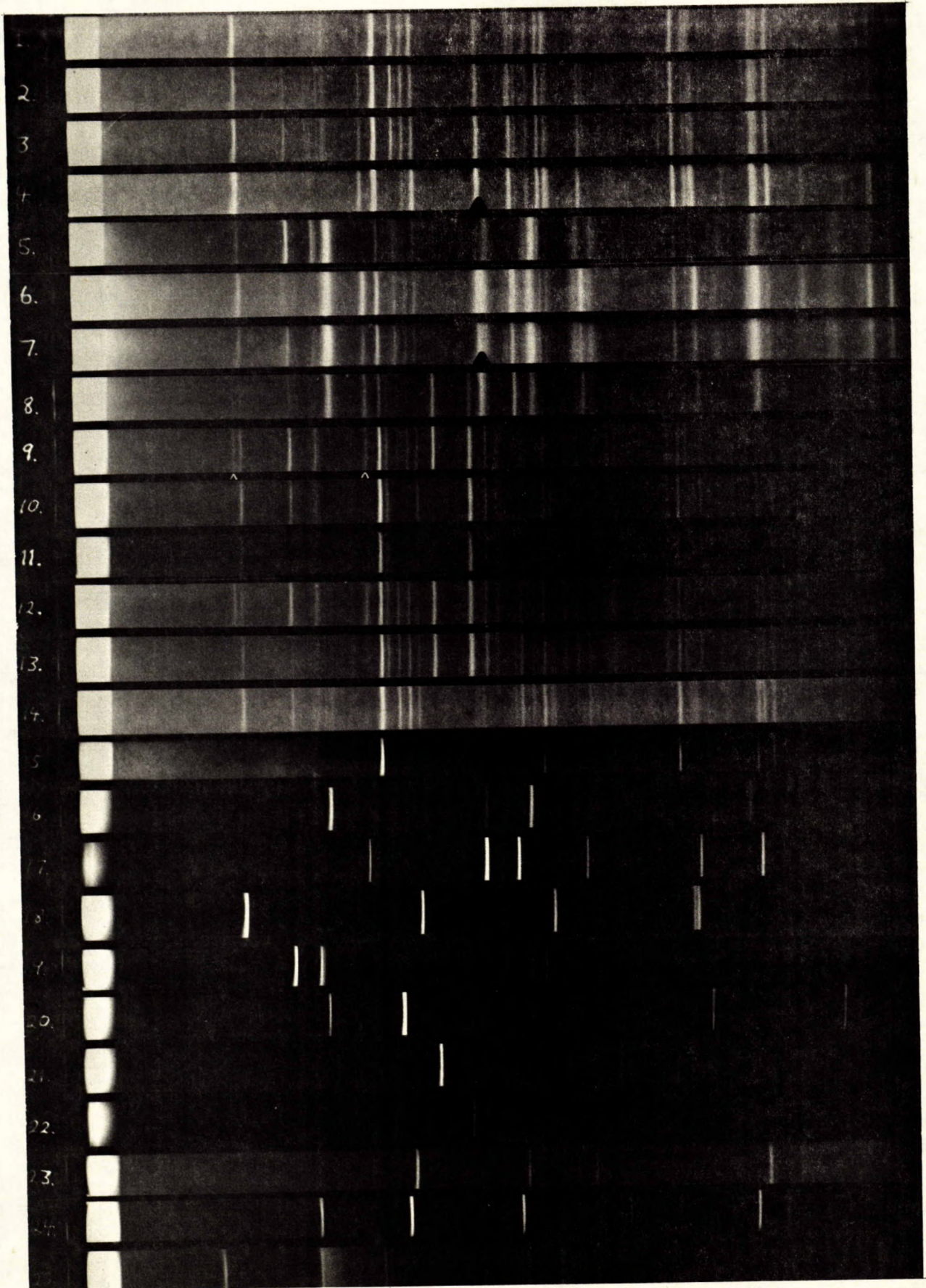


Figure 1. (See caption on facing page).

TABLE I

X-Ray Diffraction Analyses of 'Red Muds'

Sample	Constituent								
	Goethite	Hematite	Boehmite	Gibbsite	Anatase	Rutile	Quartz	Zircon	Calcite
No. 27154 February/63	F	D	C	G	B	D	E	G	-
No. 27154 July/63	F	C	D	F	B	D	D	F	-
No. 27154 October/63	F	C	D	F	B	D	D	G	-
Synthetic Mud	-	B	B	-	A	E	-	-	-
No. 22757	A	-	E	C	E	F	-	-	-
No. C-39530 ERM-265	B	A	D	-	C	F	F	-	-
No. C-39778 JRM-365	B	C	E	E	D	F	F	-	-
No. 22758	C	C	F	F	D	G	F	G*	D

Estimated abundance of constituents from "A" (very abundant) to "G" (trace).

Note that Sample No. 22758 contains other constituents which are described in text.

*Detected only in material from which iron oxides had been removed.

TABLE 2

Comparison of Determinations of Relative Abundances of
Gibbsite and Boehmite in 'Red Mud' Samples

Sample	Boehmite			Gibbsite		
	ALCAN Analyses (%Al ₂ O ₃)		Guinier Camera*	ALCAN Analyses (%Al ₂ O ₃)		Guinier Camera*
	Chemical	X-ray Diffraction		Chemical	X-ray Diffraction	
No. 27154 February/63	ND	22.1	C	8.4	2.4	G
No. 27154 July/63	ND	9.8	D	5.3	3.4	F
No. 27154 October/63	ND	14.2	D	8.0	5.7	F
Synthetic Mud	31.0		B	1.21		-
No. 22757	4.1	2.4	E	13.9	20.9	C
No. C-39530 ERM-265	3.1-4.5	2.4	D	2.6-7.8	1.1	-
No. C-39778 JRM-365	4.1-6.2	2.2	E	4.0-5.2	4.3	E
No. 22758	2.5	2.3	F	5.6	5.8	F

ND - not determined.

*Estimated abundance of constituents from "A" (very abundant) to "G" (trace).

A strong general similarity is evident between the powder patterns of the apatite standard (No. 22) and the material in Sample No. 22758. The complete dissolution of this phase in 2% acetic acid, as shown by pattern No. 14, strongly supports its identification as carbonate apatite (6, p. 327).

Reflections from one or more unidentified phases, at 6.3 and 3.66 Å, have been marked in Figure 1, pattern No. 9. A sharp intensity drop in both of these reflections was noted in the powder pattern of the 'white' fraction which had been separated from Sample No. 22758 by centrifugation (pattern No. 10). This suggests that both reflections are from a single phase which is unrelated to carbonate apatite. The investigation of the 'grey' fraction indicated that the unknown substance is soluble with some difficulty in solutions of boiling 0.5 N NaOH (pattern No. 13).

TABLE 3

Reflections Obtained from Constituents Not Listed in
Table 1; Sample No. 22758

d(Å)	Interference	X-Ray Powder Data for Carbonate Apatite (A), from Ames(5. p. 833)
6.3*		
—		4.12 (W)
3.66*	Hematite	
3.42		3.40 (M)
2.77		2.77 (S)
2.67	Hematite	2.69 (M)
2.61		2.61 (M)
2.22	Goethite	2.23 (W)
1.92		1.931 (M)
1.823	Hematite	1.834 (M)

*Reflections from unidentified constituent.

The very weak 3.66A reflection obtained from the NaOH-treated sample was attenuated still further following the 2% acetic acid treatment which completely extinguished the 6.3A reflection (pattern No. 14). However, in the case of the residual 3.66A reflection in pattern No. 14, it was suspected that this represented hematite which had survived the iron oxide removal treatment as inclusions within other mineral grains. This was supported by the discovery, in pattern No. 14, of a reflection at 2.69A corresponding to the strongest hematite line.

Despite a careful search of the ASTM X-Ray Powder Diffraction File the material within Sample No. 22758 which yielded the 6.3 and 3.66A reflections remained unidentified.

CONCLUSIONS

(1) The Guinier X-ray powder method may be used for the detection of gibbsite in 'red mud' insoluble residues when the proportion of this mineral exceeds approximately 2-3% of the whole. The low relative intensity of the powder patterns obtained from gibbsite and boehmite is due to the fact that the bulk of the 'red mud' samples are composed of iron and titanium oxides, which absorb X-radiation much more strongly than do aluminium hydroxides (7, p.414). The detection limit of boehmite will be somewhat lower than that of gibbsite, as this mineral contains a higher proportion of relatively heavy aluminium atoms.

(2) Removal of free iron oxides by the method of Mehra and Jackson (2) results in the concentration of all other phases. This preliminary treatment may be especially useful in quantitative determinations by X-ray diffraction as it would reduce most 'red mud' samples to essentially simple titaniumoxide - aluminium hydroxide systems and thus eliminate the variable matrix effects which are a major source of error in these analyses. Calcite, carbonate apatite, and the unidentified substance in Sample No. 22758 may similarly be dissolved by treatment with a solution of 2% acetic acid.

(3) The partial segregation of phases which occurs during the high-speed centrifugation of 'red mud' suspensions may aid in the identification of unknown constituents.

(4) An unidentified substance within Sample No. 22758 yielded reflections at 6.3 and 3.66A and was apparently soluble both in boiling 0.5 N NaOH solutions and in 2% acetic acid solutions at room temperature.

REFERENCES

1. P. M. deWolff, "Multiple Guinier Cameras", *Acta Cryst.* 1, 207-211 (1948).
2. O. P. Mehra and M. L. Jackson, "Iron Oxide Removal from Soils and Clays by a Dithonite-Citrate System Buffered with Sodium Bicarbonate", *Clays and Clay Minerals, Proc., Seventh National Conf. on Clays and Clay Minerals*, Pergamon Press, New York, 317-327 (1960).
3. I. Hashimoto and M. L. Jackson, "Rapid Dissolution of Allophane and Kaolinite-Halloysite after Dehydration", *Clays and Clay Minerals, Proc., Seventh National Conf. on Clays and Clay Minerals*, Pergamon Press, New York, 102-113 (1960).
4. H. P. Rooksby, "Oxides and Hydroxides of Aluminium and Iron", *The X-Ray Identification and Crystal Structures of Clay Minerals*, Mineralogical Society, London, 354-392 (1961).
5. L. L. Ames, Jr., "The Genesis of Carbonate Apatites", *Economic Geology* 54, 829-841 (1959).
6. W. A. Deer, R. A. Howie, and J. Zussman, "Rock-Forming Minerals, Vol. 5, Non-Silicates", Longmans Canada Ltd., Toronto (1962).
7. H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials", John Wiley and Sons Inc., New York (1954).