R Lancashire

Bauxite and aluminium production

The term *Bauxite* is derived from Les Baux, a town near Arles in southern France where, in 1821, Berthier obtained a sample of a red clay-like sediment, rich in aluminium. It appears that bauxite was originally considered to be a new mineral, however, later work revealed considerable variations in mineralogical composition, physical appearance and mode of occurrence. The name *Bauxite ore* is generally applied to all bauxites which contain not less than 45–50 per cent of one or more of the hydrated aluminium oxides, and not more than 20 per cent Fe_2O_3 and 3–5 per cent combined silica, and which are considered economically mineable, now or in the foreseeable future. Table 1[2] shows some of the main minerals present in bauxite deposits.

The first commercial alumina (Al_2O_3) extraction from bauxite was attributed to Henri Sainte-Claire Deville[3] about 1854, whereupon the price of aluminium quickly tumbled to a thirtieth of its price. This method soon gave way to that of Karl Joseph Bayer[4] in 1888, and the Bayer Process caused a further marked reduction in price of aluminium metal which eventually led to it becoming an everyday commodity rather than a precious metal.

The Bayer Process, which continues to be the most economical method of manufacturing alumina, is schematically summarised in *Fig. 1* and involves the following operations:
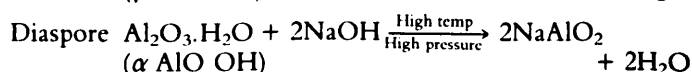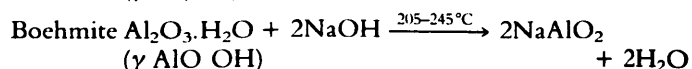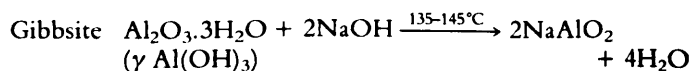
1 dissolution of the alumina at elevated temperatures;

2 addition of flocculants then separation and washing of the insoluble impurities of bauxite (red mud) to recover the soluble aluminate and caustic soda;

3 precipitation of pure Gibbsite by seeding the cooled, clarified solution with previously precipitated crystals;

4 regeneration of the solutions for recycling to step 1 by evaporation of the water introduced by the washings;

Fig. 1. The Bayer process (numbers refer to description in text).
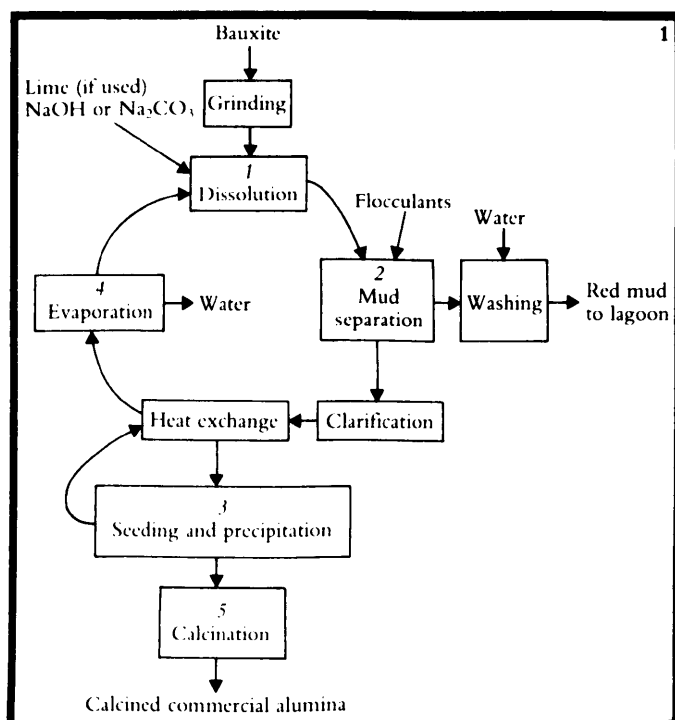
5 heating the precipitated Gibbsite, to 1100 °C (calcination) to remove the chemically combined water, hence producing alumina.

In order to remove the iron oxides and most of the silicon oxides present, the ore is first treated with aqueous sodium hydroxide. The digestion process takes advantage of the solubility of amphoteric aluminium oxides to form a solution of aluminate ions, whilst the basic iron oxide, which does not dissolve, is separated by filtration. Thus

Gibbsite $Al_2O_3.3H_2O + 2NaOH \xrightarrow{135-145°C} 2NaAlO_2$
$(\gamma\ Al(OH)_3) \qquad\qquad\qquad + 4H_2O$

Boehmite $Al_2O_3.H_2O + 2NaOH \xrightarrow{205-245°C} 2NaAlO_2$
$(\gamma\ AlO\ OH) \qquad\qquad\qquad + 2H_2O$

Diaspore $Al_2O_3.H_2O + 2NaOH \xrightarrow[\text{High pressure}]{\text{High temp}} 2NaAlO_2$
$(\alpha\ AlO\ OH) \qquad\qquad\qquad + 2H_2O$

Complete extraction from diasporic bauxite requires stronger caustic solutions, in addition to higher temperatures and pressures. In general, the reaction equilibria above move to the right with increases in caustic soda concentration and temperature. The actual conditions employed at each process plant are determined by the types of bauxite most commonly encountered there. In practice this means that for deposits containing the more easily recoverable Gibbsite only, production costs are much lower than when Boehmite or Diaspore are present.

The control of silica in the conventional Bayer process is most important and, in fact, ores having reactive silica greater than 7 per cent cannot be economically processed.

Unlike quartz, which is considered virtually non-reactive at Gibbsite extraction temperatures, some minerals, including kaolins, dissolve rapidly and the reaction of the silica can give rise to appreciable loss of caustic soda and aluminium.

The control of silica[5] is generally carried out during, or prior to, the digestion step, and generally involves dissolution, eg for kaolin

$$Al_2O_3.2SiO_2 + NaOH \longrightarrow Na_2SiO_3$$

and desilication via precipitation,

$$Na_2SiO_3 + NaAlO_2 \longrightarrow Na_2O.Al_2O_3.2SiO_2$$
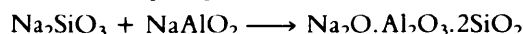
Dissolution is necessary to supersaturate the liquid to a point where the sodalite formed acts as a seed to precipitate more sodalite. The rate of precipitation is found to increase with temperature, however at 135–150 °C it is significantly slower than is required for complete Gibbsite extraction which occurs within minutes. The need for desilication

Table I. Main Minerals of Bauxite Deposits.[2]

| Name	Composition
Gibbsite (Hydrargillite)	$\gamma - Al(OH)_3$, $\alpha - Al_2O_3.3H_2O$
Boehmite	$\gamma - AlOOH$, $\alpha - Al_2O_3.H_2O$
Diaspore	$\alpha - AlOOH$, $\beta - Al_2O_3.H_2O$
Hematite	$\alpha - Fe_2O_3$
Goethite	$\alpha - FeOOH$
Magnetite	Fe_3O_4
Siderite	$FeCO_3$
Ilmenite	$FeTiO_3$
Anatase	TiO_2
Rutile	TiO_2
Brookite	TiO_2
Halloysite	$Al_2O_3. 2\ SiO_2.3H_2O$
Kaolinite	$Al_2O_3.2SiO_2.2H_2O$
Quartz	SiO_2

therefore means that material must be held at the digestion temperature long enough to allow the silica to precipitate.

The insoluble residues remaining after digestion (red mud) contain iron oxides, sodium aluminium silicate, titanium oxide and various other metal oxides. Disposal of the washed muds is a major problem and these are generally lagooned. It has been estimated[6] that approximately 1 km^2 of lagoon area is required for a plant processing 3.3m t of bauxite per year; however, the same lagoon may be used for several years. Much research has been directed toward extraction of various elements from the red mud, but no economic process has yet been developed. There have also been attempts to convert the mud into building products and cements. However, a report[7] recently prepared for the US Environmental Protection Agency concerning the use of red muds, concluded that there was no possibility for utilising the muds that could significantly reduce the need for impoundment in the near future.

Production of aluminium

In 1886, Hall and Héroult[8], working independently, simultaneously discovered that electrolysis of molten cryolite (Na$_3$AlF$_6$) in which alumina was dissolved, led to the formation of metallic aluminium. The Hall–Héroult process[6] is still the basis for which nearly all aluminium is produced. In the modern process, a little fluorspar (CaF$_2$), aluminium fluoride (AlF$_3$) and lithium fluoride (LiF) are added with the alumina to reduce the melting point of the cryolite and improve the efficiency. Carbon anodes and cathode are used; the aluminium metal is deposited onto the cathode which is also the melt container, while oxygen is evolved at, and consumes, the anode forming CO$_2$ which escapes as gas. (Fig. 2).

It is believed that during electrolysis, cryolite ionises to form AlF$_6^{3-}$ which dissociates to AlF$_4^-$ and F$^-$ thus:

$$Na_3AlF_6 \longrightarrow 3Na^+ + AlF_6^{3-}$$
$$AlF_6^{3-} \rightleftharpoons AlF_4^- + 2F^-$$
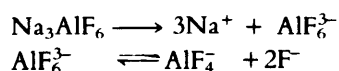
Alumina then dissolves at low concentrations according to the following reactions:

$$Al_2O_3 + 4AlF_6^{3-} \longrightarrow 3Al_2OF_6^{2-} + 6F^-$$
$$Al_2O_3 + AlF_6^{3-} \longrightarrow 3AlOF_2^-$$

At the cathode where aluminium is deposited, hexafluoroaluminate ions are discharged

$$4AlF_6^{3-} + 12e^- \longrightarrow 4Al + 24F^-$$
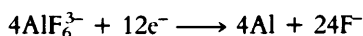
whereas at the anode, the oxyfluoride ions discharge forming CO$_2$ and reforming AlF$_6^{3-}$ ions, thus

$$6AlOF_2^- + 3C + 24F^- \longrightarrow 3CO_2 + 6AlF_6^{3-} + 12e$$
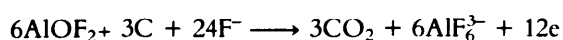
The overall cell reaction can therefore be written as:
$$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$$
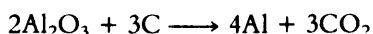
An interesting feature of the electrolysis is given by the thermodynamic data[9]. The energy changes occuring are:

$$Al_2O_3 \xrightarrow{electrolysis} 2Al + \tfrac{3}{2}O_2 \qquad \Delta G_{1260K} = 1255\,kJ$$
$$\tfrac{3}{2}O_2 + \tfrac{3}{2}C \longrightarrow \tfrac{3}{2}CO_2 \qquad \Delta G_{1260} = -603\,kJ$$

consequently, for the overall process

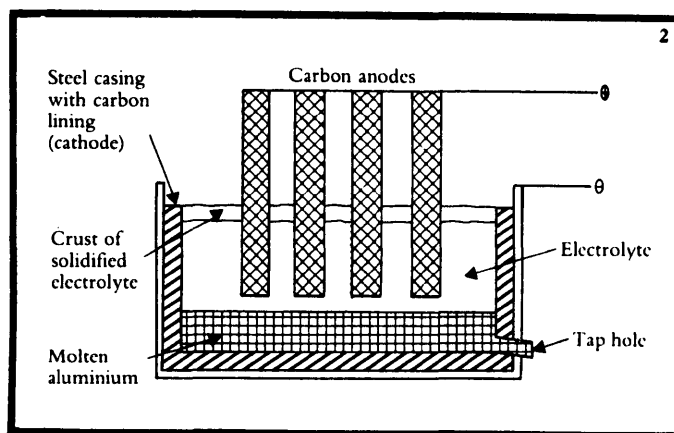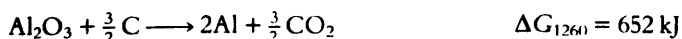$$Al_2O_3 + \tfrac{3}{2}C \longrightarrow 2Al + \tfrac{3}{2}CO_2 \qquad \Delta G_{1260} = 652\,kJ$$

Fig. 2. The Hall–Héroult electrolytic cell.

That is, the consumption of the carbon anodes during the electrolytic extraction, reduces the total energy input required by nearly a half.

Whilst aluminium is second only to iron as the most abundant of the metals used by man, it is relatively difficult to separate from its parent rock. The rapid growth of the aluminium industry in the 20th century has been founded on

Table 2. Aluminous minerals constituting potential sources of alumina.[13b]

| Mineral	Formula	Wt per cent Al$_2$O$_3$	Occurrence
Mullite	Al$_6$Si$_2$O$_{13}$	72	Rare naturally, but common in fly ash
Andalusite Sillimanite Kyanite	Al$_2$SiO$_5$	63	Metamorphic minerals
Staurolite	Fe$_2$Al$_9$O$_6$(SiO$_4$)$_4$(O,OH)$_2$	Up to 54	Metamorphic mineral
Kaolinite	Al$_2$O$_3$.2SiO$_2$.2H$_2$O	39.5	Alteration of feldspar
Muscovite	K.Al$_2$(AlSi$_3$O$_{10}$)(OH)$_2$	Up to 38	Metamorphic, igneous or pegmatitic mineral
Alunite	K.Al$_3$(SO$_4$)$_2$(OH)$_6$	37	Alteration product of near-surface volcanic rocks
Plagioclase	(Na,Ca)(Al,Si) AlSi$_2$O$_8$	20 to 36	Common constituent of igneous rocks
Dawsonite	NaAl(OH)$_2$CO$_3$	35	Rare diagenetic mineral
Nepheline	(K, Na)AlSiO$_4$	32	Common constituent of alkaline igneous rocks
Pyrophyllite	Al$_4$(Si$_8$O$_{20}$)(OH)$_4$	28	Alteration of feldspar
Leucite	K(AlSi$_2$O$_6$)	23	Rare igneous mineral
Montmorillonite	Al$_4$(Si$_4$O$_{10}$)$_2$(OH)$_4$	c20	Alteration of feldspar
Illite	K.Al$_4$(Si$_{8-y}$Al$_y$)O$_{20}$(OH)$_4$.nH$_2$O	c20	Alteration of feldspar
Crandallite	CaAl$_3$(PO$_4$)$_2$(OH)$_5$.H$_2$O	19.6	Leached phosphoric sand
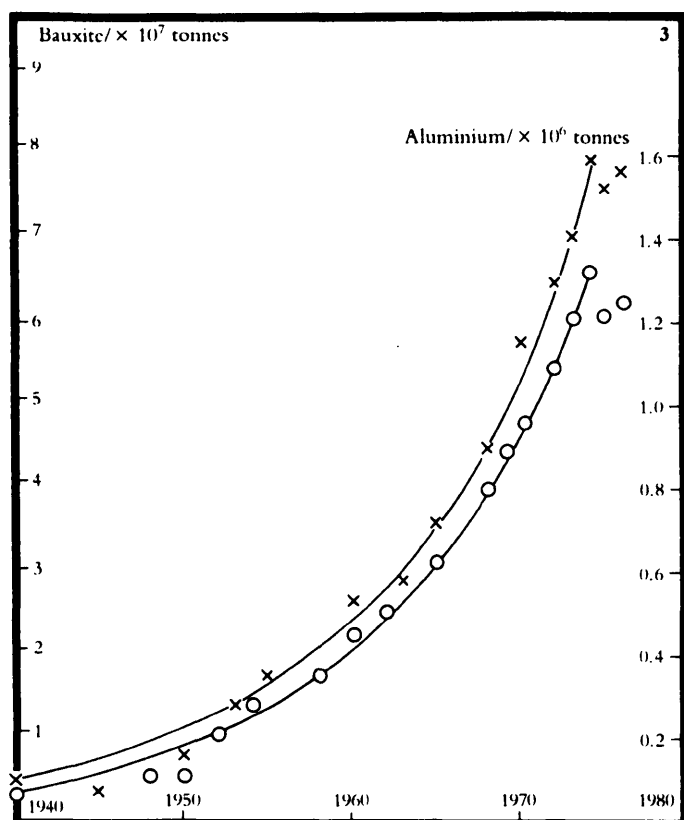
Fig. 3. World bauxite and aluminium production: ×, bauxite; ○, aluminium.

a number of rich bauxite deposits. In brief, bauxite is the product of *in situ* weathering during which components such as soda, potash, lime, magnesia and some silica were removed in solution from the parent rock. This process required a warm humid climate of continuous moisture so that rich deposits are largely found in tropical or sub-tropical regions.

Figure 3[10] shows the dramatic increase in bauxite and aluminium production over the past 40 years. The discontinuity of these graphs at 1974–1975 coincides with the creation of the International Bauxite Association(IBA). The majority of the world's bauxite now comes from the member countries of IBA, who in 1974 introduced significant increases in tariffs and taxation. It has been claimed[11] that these price increases led to some countries, particularly those with large aluminium industries and small bauxite deposits, accelerating their prospecting and research activities to consider itilising indigenous aluminium-bearing minerals for aluminium production. However, the US for example, still imports over 90 per cent of its bauxite. The situation with bauxite is not unique, since the US also imports 90 per cent or more of manganese, cobalt and chromium needs.[12]

Alternatives to bauxite and the Bayer process

Non-bauxite sources of aluminium are not a new option. There are a large number and vast quantities of aluminium-bearing minerals and rocks. However, while most of these comprise silicates, which are resistant to chemical dissolution and extremely difficult to process, some are considered to constitute potential sources of alumina (see Table 2).[13b]

The early work on non-bauxite sources was prompted by the potential disruption of bauxite supplies during World War II. At that time Germany for example, used domestic clay and

andalusite as a minor source of aluminium.

After World War II, the aluminium industry relied almost entirely on bauxite as a raw material, and there was neither reason nor incentive to pursue alternatives.

The presently known world bauxite reserves and resources and their geographical distribution are given in Table 3,[13] together with the 1979 production estimates for the western world.[14] The reserves exist in sufficient quantities to satisfy normal requirements for 50–100 years. In addition, because of the need to avoid medium-term shortages, it is believed that both the US and USSR have stockpiled sufficient bauxite to meet their needs for at least 12 months.

Despite this, however, it is considered that these reserves and resources are less secure and economically attractive than

Table 3. World bauxite reserves: resources[13a] and estimated western world production figures for 1979[14] (figures in million tonnes).

Countries		Reserves	Resources	Production
North America				
United States		40	400	1.7
Caribbean & Central America				
Costa Rica		120	100	–
Dominican Republic		40	20	0.5
Haiti		10	60	0.6
Jamaica		1,600	800	0
	Subtotal	1,770	980	12.0
South America				
Brazil		4,070	30,000	1.4
Colombia		–	70	–
French Guiana		–	1,700	–
Guyana		1,810	25,000	3.0
Suriname		500	10,000	5.0
Venezuela		500	1,500	–
	Subtotal	6,880	68,270	
Africa				
Cameroon		1,500	10,000	–
Ghana		250	300	0.3
Guinea		11,500	10,000	12.0
Sierra Leone		400	300	0.7
	Subtotal	13,650	20,600	
Asia				
India		1,100	1,000	2.1
Indonesia		700	2,000	1.0
Malaysia		50	15	0.3
Turkey		50	200	0.2
	Subtotal	1,900	3,215	
Europe				
France		30	200	2.0
Greece		450	300	2.7
Hungry		200	200	–
USSR		300	300	–
Yugoslavia		200	500	2.9
	Subtotal	1,180	1,500	
Oceania				
Australia		5,000	6,000	26.1
Solomon Islands		60	100	–
	Subtotal	5,060	6,100	
Others		300	7,000	
Total		30,780	108,065	74.5

Reserves = Measured, indicated and inferred reserves.
Resources = Identified sub-economic and undiscovered resources.
Production figures for western world only.

they once were. Coupled to this are increased costs and drawbacks related to the Bayer process such as the need to process ores of a particular quality (high extractable alumina (40–60 per cent), low reactive silica (< 7 per cent)), and the problems of red mud disposal. These factors have led to renewed interest in non-bauxite sources of aluminium.

The only peace-time aluminium industry based partly on the use of non-bauxite materials is in the USSR, where alunite and nepheline concentrate are used as the raw materials. Nepheline concentrate cannot be directly compared with other non-bauxite sources since it is not a crude ore but a by-product in the production of apatite for fertilizer.

The experimental processes currently in operation either at industrial scale or pilot-plant include:[11,15,16]

1. Pechiney-Ugine-Kuhlmann (H-plus process) (French)
2. Cirzymek (Polish)
3. Nitric Acid – ion exchange (American)
4. Hydrochloric acid – isopropyl ether extraction (American)
5. Lime – soda sinter (American)
6. Nepheline concentrate (Soviet Union)

Of these, the Pechiney H-plus process[11a,17] is the nearest competitor to the Bayer process in terms of running costs and energy requirements. This process, which can utilise a variety of raw materials ranging from clay and kaolin to tailings from coal mines with alumina contents as low as 20 per cent; involves the following steps:

a crushing of the raw material
b digestion in 60–70 per cent H_2SO_4 at 130–140 °C
c filtration and recrystallisation of aluminium sulphate
d introduction to the solution of anhydrous HCl
e cooling and crystallisation of aluminium chloride
f filtration and calcination to form alumina.

The extraction efficiency of these alternative processes are usually lower than for the Bayer process and in general much

A Cryolite crystal.

more energy is required to extract the same quantity of alumina.

In conclusion, the following factors should ensure that bauxite retains its position as the primary aluminium ore for the foreseeable future:
● the existence of adequate reserves
● the present state and potential for future development of the Bayer–Hall–Héroult technologies
● extraction of by-products, for example, vanadium and gallium. Gallium[18] is recovered from the aluminate liquor in countries including US, France, Germany and Hungary, and Bayer liquor extractions represent the major source of the world's supplies of this increasingly useful element.

The US aluminium industry is committed to the use of bauxite as its source of primary aluminium for the following reasons:
● it is based on Bayer processed bauxite and changes to another process and material would involve major changes in technology;
● it has major overseas investments in the mining and processing sectors and in shipping installations;
● the present industry–government joint ownership of mines and other installations in some countries is based on long-term agreements;
● it is only with high government subsidy that the aluminium industry would be able to use non-bauxite aluminous raw materials.

Consequently it is unlikely that within the next 20–30 years that aluminium companies will need to heed the words of Sir Fred Hoyle[19] and 'simply turn to clay'.

Dr Robert Lancashire is a lecturer in inorganic chemistry at the University of the West Indies, Jamaica.

References

1 P. Berthier, *Ann. Mines*, 1821, **6**, 531.
2 I. Valeton, *Development of Soil Science I Bauxites*. Elsevier Publishing, 1972.
3 H. Sainte-Claire Deville, *Ann. Chim. Pys.*, 1854, **43**, 27. *Compt. Rend.*, 1854, **46**, 452.
4 K. J. Bayer, *Chem. Zeitung*, 1888, **12**, 1210.
5 R. A. Meikle, *Journal of the Geological Society of Jamaica Proceedings of Bauxite Symposium, No II*, 3 Oct, 1973, p 30.
6 *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd edn, Vol 2. Wiley-Interscience, 1978.
7 B. K. Parekh and W. M. Goldberger, *U.S. Environmental Protection Agency Technology Series, EPA-600/2-76-301*, Dec 1976.
8a *The Aluminium Industry in Brief*. Alcan Jamaica, 1969.
8b O. A. Battista, *Chemistry*, 1969, **42**, 14.
9 J. W. Moore and E. A. Moore, *Environmental chemistry*, 275–276. Academic Press, 1976.
10 *Year-Book of American Bureau of Metal Statistics*, 1976.
11a N. A. Shaikh, *2nd 'Industrial Minerals' international conference report from Munich*, 1976.
11b S. H. Patterson, *American Scientist*, May-June (1977).
12. U.S. Bureau of Mines, *AIME Conference*, Feb 1980.
13a V. G. Hill in *Journal of the Geological Society of Jamaica*, Special issue, Proceedings of Bauxite Symposium IV, pp 3–19 June, 1980.
13b N. W. Bliss in *Journal of the Geological Society of Jamaica*, Special Issue, Proceedings of Bauxite Symposium IV, pp 201–226, June 1980.
14 *Mining Annual Review*, 1980.
15a P. W. Johnson, F. A. Peters and R. C. Kirby, *U.S. Bureau of Mines Report of Investigation 6431*, 1964.
15b F. A. Peters and P. W. Johnson, *US Bureau of Mines Information Circular 8648*, 1974.
16 G. Parkinson, *Chemical Engineer (UK)* 1971, **78**, 83.
17a *Chemical Week*, 1974, March, **40**.
17b J. A. Osborne, *Proceedings of the Royal Aust. Chem. Inst.*, 1977, **44**, 31.
18 *Chemicals and technology: an encyclopedic treatment, Vol 3, Metals and ores.* Barnes and Noble, 1970.
19 F. Hoyle, *Energy or extinction —the case for nuclear energy.* London: Heinemann, 1977.