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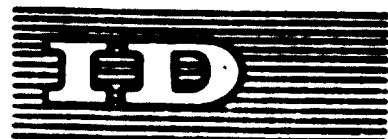
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TECHNICAL ASPECTS OF ALUMINA PRODUCTION
FROM COMPLEX ORES ^{1/}

by

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^{1/} The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the Secretariat of UNIDO.

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Introduction

1. Since 1956 aluminium production has been second only to that of cast iron and steel, in terms of quantity. In 1963, world aluminium output was 6,739,000 tons, 39 per cent higher than in 1959. By 1975 the United States alone is planning to attain an output of 6.6 million tons of aluminium per year.
2. This rapid rise in aluminium production, which has been surpassed in rate of growth only by the production of lithium, gives reasonable grounds for doubting whether future supplies of raw materials will be sufficient. A number of countries that lack bauxite, the basic raw material, are already engaged in research and are making preliminary plans for the production of aluminium from materials other than bauxite.
3. The known reserves of bauxite in the world (outside the Union of Soviet Socialist Republics) amount to some five billion^{1/} tons, and this figure is not likely to grow much larger, because the deposits on the surface of the earth's crust have already been thoroughly explored. It is unlikely that deep-lying deposits will be found, considering the conditions under which bauxite is formed. Considering also the way bauxite extraction and processing are developing, the world resources of this commodity are not vast and will be used up in the next few decades. At that time the aluminium industry will have to be adapted to other types of raw materials.
4. Before considering the various types of raw materials other than bauxite, it should be noted that bauxites themselves are not entirely homogeneous materials. They can be divided into two basic groups: residual and sedimentary. Residual bauxites are formed by the process of weathering into laterite of various rocks, including basalt, and they are found at the place of their original formation, covering their matrices. Sedimentary or secondary bauxite deposits are formed by leaching or transfer from their matrices, where, however, they are also found in lenses. A total of 42 chemical elements and some 100 minerals have been found in bauxites. Bauxite composition varies not only from deposit to deposit but also within a single deposit.

^{1/} Throughout this document the term "billion" signifies one thousand million.

5. It may be noted, at this point, that matrices of volcanic origin can be considered generally as nature's almost inexhaustible storerooms of riches. They are, as it were, the lower storey of the earth's crust, the upper storey of which is the granite layer, as it is called in geophysical terminology. The total aluminium content of the earth's crust is 7.5 per cent by weight - considerably more than the iron content. Thus, while natural forces break down the rocks of the earth's surface with the passage of the various geological epochs, liberating the raw materials needed by man together with many impurities, contemporary science and technology will very soon devise incomparably faster methods, undoubtedly giving a higher degree of purity, for the separation of alumina from basalt and similar rocks.
6. The chemical composition of basalt is, on the average, as follows: 40 to 50 per cent silicon, approximately 15 per cent aluminium, 7 per cent calcium, 6 per cent iron, 5 per cent magnesium and 2 per cent titanium. In addition, basalt contains a certain amount of alkali metals and other chemical elements, including some that are rare and precious. According to research carried out on basalts in India, their aluminium content decreases in proportion to the depth of the deposit.
7. Compared with the richer ores, the number of component elements in basalt may seem small, but basalts contain a number of useful ingredients, the comprehensive extraction of which - if cheap energy and technology are available - is an economically sound project. As an illustration, it may be noted that the mechanical processing of granite, basalt and other hard rocks into building, monumental and industrial components by sawing, which was expensive and slow but was until very recently the only method known, can now be replaced by the cheap blowtorch method. Moreover, the harder the rock the more effective the new method is.
8. In his day, the world-renowned D.I. Mendeleev put forward the view that solar energy is most effectively used on the earth for the accumulation of marsh plants and peat, which can renew fuel resources in a very short time without human intervention, and if this process were developed, it could be speeded up even further. It must therefore be assumed that if there is a specific need for this, modern science will be able to accomplish the artificial "dismantling"

of rocks to separate out purer alumina than that liberated by nature over tremendously long periods.

9. Basalt is already being used as a raw material for melting and casting into a number of useful articles which used to be cast from other materials and metals. Evaporation melting by means of plasma burners makes it easy to break down even basalt into its components, and by introducing the necessary chemical elements into the process it is also possible to obtain new materials in this way.

10. Because of its chemical composition, basalt is the most suitable raw material for the production of pyrocerams, glass-like crystalline materials which are a recent invention potentially as important as the discovery of how to make steel was in its time. Pyrocerams are very similar to aluminium in density (2.6 to 2.65 and 2.7), but they surpass it in strength, resistance to atmospheric corrosion and in value.

11. It has recently been discovered that aluminium is present in 268 minerals, but the only ones that may be considered as ores for the production of alumina or other aluminium compounds are nepheline and the rocks that contain it, aluminates, clays and kaolins, high aluminium-content silicates and, more rarely, aluminium sulphates such as pickeringite and alunogen. The chemical composition of these minerals is given in table 1.

1. METHODS FOR THE PRODUCTION OF ALUMINA FROM RAW MATERIALS OTHER THAN BAUXITE

12. There are several hundred known methods of producing alumina. This large number of methods is due to the variety of aluminous materials and to the amphoteric properties of aluminium oxide. The best known methods for producing alumina are usually divided into three groups: (a) electro-thermal, (b) acid and (c) alkaline. Naturally this classification is applicable chiefly to the processing of bauxites, which are at present the predominant raw materials in the alumina industry.

13. In the electro-thermal process, alumina is obtained by melting the ore with a reducing agent in electric furnaces. This method is not widely used, since it can only be economic when very cheap electric power is available. Furthermore, the alumina produced is not always of satisfactory quality. In the acid process,

the raw material is treated with a solution of one of the mineral acids, giving a corresponding soluble aluminium salt, while leaving the bulk of the raw material undissolved. (unfortunately, however, salts of iron and titanium frequently dissolve as well and thus impede the process). After extraction, the aluminium salt is broken down and solid aluminium hydroxide is obtained, which, after calcining, yields alumina. This acid process calls for a costly acid-proof plant, and consequently it is seldom adopted nowadays.

Table 1
Principal minerals containing aluminium

<u>Name of mineral</u>	<u>Chemical formula</u>	<u>Alumina content (%)</u>
Corundum	Al_2O_3	100
Diaspore, boehmite	$Al_2O_3 \cdot H_2O$	85
Gibbsite (hydrargillite)	$Al_2O_3 \cdot 3H_2O$	65.4
Cyanite, andalusite, sillimanite	$Al_2O_3 \cdot SiO_2$	63.2
Kaolinite	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	39.5
Alunite	$(K_x \cdot Na_y)_2 SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$	37-39
Nepheline	$(Na_x K_y)_2 O \cdot Al_2O_3 \cdot 2SiO_2$	36-32
Leucite	$K_2O \cdot Al_2O_3 \cdot 2SiO_2$	23.5
Anorthite	$CaO \cdot Al_2O_3 \cdot 2SiO_2$	36.7
Gryolite	$Na_3 \cdot Al \cdot F_4$	23.5
Orthoclase	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	18.4
Albite	$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	19.3
Beryl	$3BeO \cdot Al_2O_3 \cdot 6SiO_2$	14.0
Chrysoberyl	$BeO \cdot Al_2O_3$	80.0
Spodumene	$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	28.0
Pollucite	$Ca_2O \cdot Al_2O_3 \cdot 4SiO_2$	14.0
Pickeringite	$Mg \cdot Al_2(SO_4)_4 \cdot 22H_2O$	11.9
Alumogen	$Al_2(SO_4)_3 \cdot 16H_2O$	16.4

14. Wide use is made of the more economic alkaline process, which may be carried out in a cheap iron plant, and in which recovery of the alkali is a simple matter. In this process, the raw material is treated to produce sodium aluminate, which can be broken down into aluminium hydroxide. The final stage of the process is to calcine to aluminium hydroxide, thus producing alumina.

15. In this process, the oxides of iron, titanium and calcium do not, in practice, dissolve out of the raw material. Only the presence of silica complicates the processing of the raw material, which must therefore be selected with low silica content if it is to be treated by this method.

II. TECHNICAL QUALITY OF ALUMINA

16. The quality of alumina, most of which is intended for processing into metallic aluminium, should be approximately as follows:

Table 2
Quality of alumina (according to USSR classification)

<u>Impurities</u>	<u>Maximum permissible percentage content of impurities</u>						
	<u>Quality:</u>	<u>a₀₀</u>	<u>a₀</u>	<u>a₁</u>	<u>a₂</u>	<u>a₃</u>	<u>a₄</u>
SiO ₂		0.06	0.08	0.15	0.25	0.40	2.0
Fe ₂ O ₃		0.03	0.03	0.04	0.05	0.6	1.0
Na ₂ O		0.5	0.6	0.6	0.6	0.7	0.8
Other		1.0	1.0	1.0	1.2	1.5	2.0

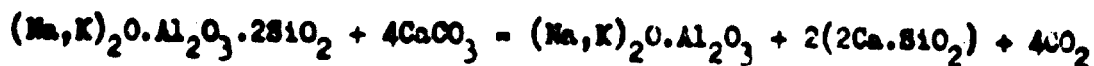
17. The presence of electro-positive and electro-negative impurities is not permissible. Similarly, the amounts of moisture and water of hydration should not exceed the permissible maxima. The dimensions of the alumina particles must be within the range of 50 to 80 microns. Only the first three qualities of alumina are used for the production of aluminium.

The technology of nepheline processing

18. Nepheline is one of the apatite-nepheline and urtite rocks used at present in the Union of Soviet Socialist Republics for alumina production. These rocks consist of two minerals: apatite $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ and nepheline $(\text{Na.K})_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, plus a certain quantity of secondary minerals. The raw material is concentrated by flotation, in the course of which the phosphatic material, apatite and its tailings, is separated from the nepheline concentrate. The most detrimental impurities are iron compounds.

19. It has been found, in practice, that for the full conversion of the alumina contained in nepheline concentrates into sodium and potassium aluminates, there should be two moles of CaO to one mole of silicon oxide in the charge. The

optimum temperature for sintering is approximately 1,300°C, and the decomposition of nepheline by the limestone takes place according to the reaction:



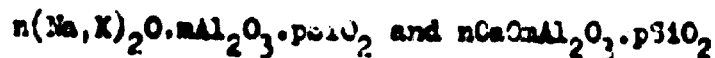
Microscopic analysis of sinter cake obtained under optimum conditions shows that it consists of dicalcium silicate and of a solid approximately 30 per cent solution of this silicate in a mixture of alkaline aluminates.

Table 3
Method of sintering (diagram of process)

Chemical composition of some nepheline rocks and their concentrates

<u>Rock/concentrate</u>	<u>Content in per cent</u>								
	<u>SiO₂</u>	<u>Al₂O₃</u>	<u>Fe₂O₃</u>	<u>R₂O</u>	<u>CaO</u>	<u>TiO₂</u>	<u>MgO</u>	<u>P₂O₅</u>	<u>Other substances</u>
Nepheline-syenite	44.35	22.45	10.00	3.47	8.33	0.77	1.12	0.5	4.8
Tailings left after concentration of nepheline-apatite	42.50	22.08	7.02	16.7	5.0	2.1	1.4	1.2	1.1
Concentrate of tailings	43.1	29.2	3.4	18.5	1.7	0.15	0.6	0.2	1.3

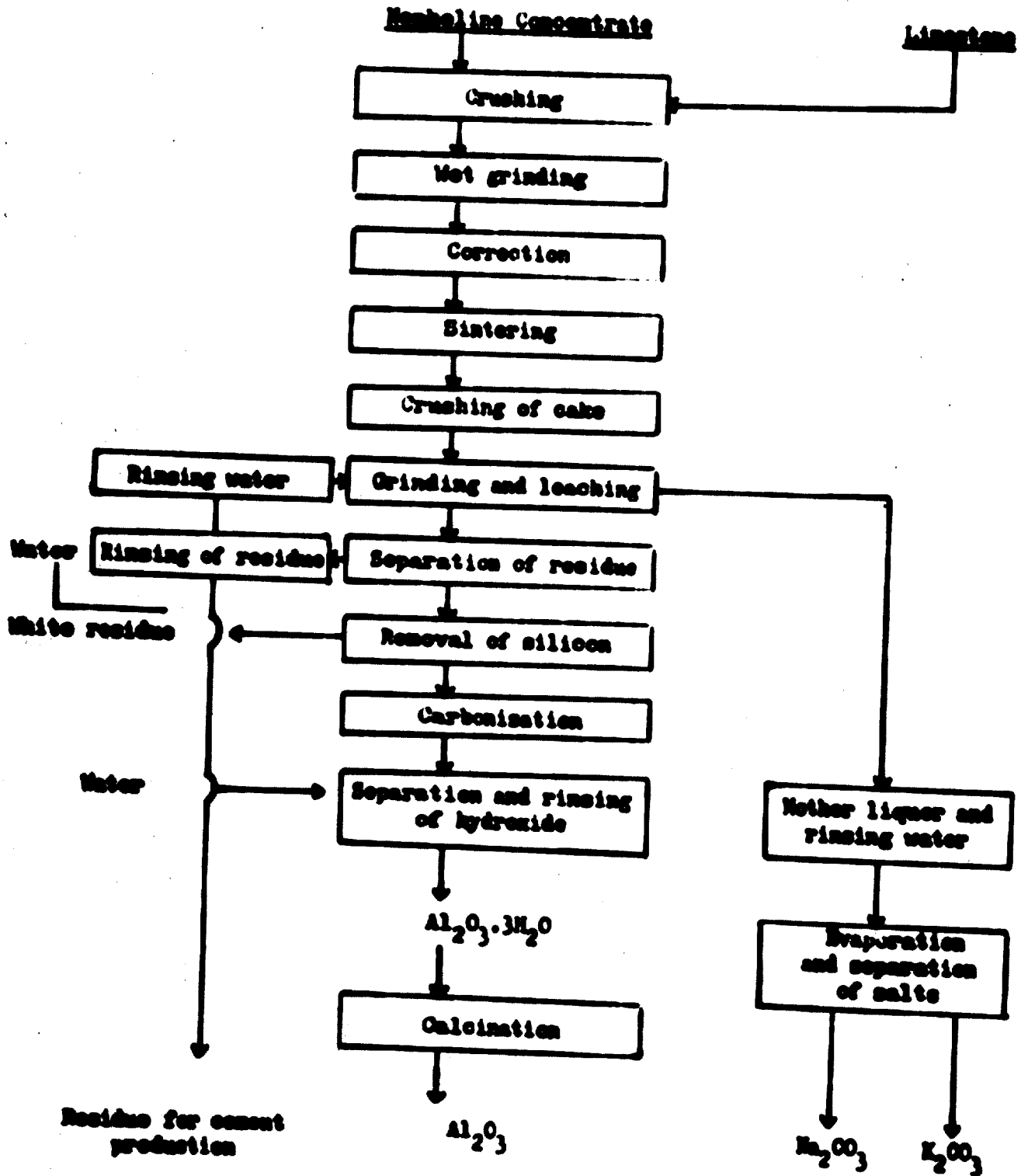
20. Where there is deviation from the optimum sintering temperature - for example, when sintering is carried out at a lower temperature - the nepheline cake produced contains, in addition to the above-mentioned products, a certain amount of undecomposed nepheline and intermediate tertiary compounds of the type:



Since these compounds are insoluble in water, they represent a waste of alkali and alumina.

21. Deviation from the optimum composition of the nepheline-limestone charge is equally detrimental. Thus, for example, the inclusion of more limestone in a batch than is called for by the formula for the formation of dicalcium silicate may give cake from which only a reduced quantity of alumina can be extracted upon leaching. This has to do with the formation during sintering of highly alkaline calcium silicates which, during leaching, generate free lime which partially reacts with the aluminate solution and returns a portion of the alumina to the

Table 4
General technological diagram of the process for
sintering nepheline raw material



insoluble state. On the other hand, an insufficient amount of limestone in the charge leads to incomplete breakdown of the nepheline and to a lower yield of alumina and Na_2O .

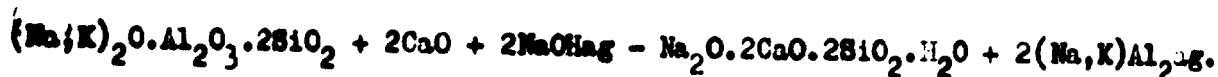
Table 5
Practical effect of the sintering temperature
of the nepheline charge on the properties of the
cake and the yield of the leaching process

<u>Sintering</u> <u>temperature, °C</u>	<u>Specific</u> <u>gravity</u>	<u>Porosity</u> <u>%</u>	<u>Extraction from cake</u>	
			Al_2O_3	Na_2O
1250	2.94	46	79.5	79.3
1270	2.96	31	82.9	80.4
1290	2.99	20	84.6	85.2
1300	3.05	13	86.0	87.1
1310	3.10	7	87.5	86.9
1330-1360	3.110	6	89.0	90.0

22. The consumption of heat, for a charge humidity level of 26 to 28 per cent and using pulverised coal heating, is 1,300 kilocalories per kilogram of cake. A diagram showing the technological process for treating nepheline is given above.

The new hydrochemical method (14)^{3/}

23. In the new hydrochemical method for breaking down nephelines by means of a solution of caustic soda in the presence of calcium oxide, with heating up to 200-280° in an autoclave, the reaction is as follows:



24. This reaction results in the formation of alkaline aluminato, which goes into solution. In establishing the technique for this method, nepheline composed of Al_2O_3 - 33.3%; Na_2O - 15.43%; K_2O - 6.47%; SiO_2 - 42.22%; Fe_2O_3 - 1.2% and CaO - 0.9% was treated in 3, 6, 10 and 13 N solutions of NaOH (i.e. containing 94.8; 194.4; 326.9 and 424.5 grams of Na_2O per litre, respectively) in the presence of CaO for exposure times of 0.2, 5, 10 and 30 minutes at temperatures of 200° and 280°C in an autoclave, the heating rate being 5° per minute. The amount of CaO was determined on the basis of the SiO_2 content, taking a molecular ratio of $\text{CaO}:\text{SiO}_2 = 1.0$. The estimated caustic module - molecular ratio, $\text{R}_2\text{O}:\text{Al}_2\text{O}_3$, was 12.0.

^{3/} Numbers in parentheses refer to the bibliography.

25. The breakdown of the nepheline and the formation of new phases ends during the period of heating up to 280° or during the first five to ten minutes of leaching at that temperature. The degree of alumina extraction is 88 to 90 per cent. In the opinion of research workers, this method is also suitable for breaking down other alumo-silicates.

Techniques for the processing of aluminium silicates

26. The possibility of using clays and kaolins as raw materials for alumina production is being given much study, but the technical conditions under which these materials might be suitable for alumina production have not yet been worked out in detail. The best clays and kaolins for this purpose appear to be those with a composition approaching the theoretical composition of kaolinite. The best quality materials would therefore be secondary kaolins; the suitability of other deposits for the extraction of alumina would depend on their concentration possibilities.

27. Kaolins can be converted into alumina by two methods: sintering and acid treatment. For processing by the acid method, kaolins must have the smallest possible ferric oxide content, at any rate not exceeding 2 to 3 per cent; those with an alumina content of not less than 30 to 32 per cent are considered suitable for processing by the sintering method.

28. Silicates with a high aluminium oxide content, such as andalusite, cyanite, sillimanite and diaspore-containing clays, may be converted into alumina by the electro-thermal method. However, they are subject to special requirements regarding their content of such impurities as Fe₂O₃, TiO₂, CaO, MgO, Na₂O and K₂O, and consequently only their concentrates are processed. In the Union of Soviet Socialist Republics a provisional technique has been devised for treating this type of raw material.

	<u>For concentrates of high-alumina silicates</u>	<u>For concentrates of argillaceous minerals</u>
	%	%
Al ₂ O ₃ not less than	59	38
SiO ₂ not more than	37.5	47
Fe ₂ O ₃ not more than	1.5	0.5
TiO ₂ not more than	1.2	0.3
Na ₂ O + K ₂ O not more than	0.7	0.5
CaO + MgO not more than	0.6	0.6
Other substances	-	14

29. To obtain alumina from clays, kaolins, coal-ash and other silicates by the sintering method, these materials are sintered with limestone in such a way as to produce spontaneously disintegrating alumo-calcium sinter cake. The amount of limestone in the charge is such as to bring about the formation of the compounds $2\text{CaO}\cdot\text{SiO}_2$ and $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$. The charge components are first ground in a wet ball mill to a particle size of approximately 0.088 mm. The wet charge then goes into a rotary furnace where it is sintered at a temperature of 1,375 to 1,425°C. The necessary completeness of interaction between the components of the charge and the requisite property of spontaneous disintegration of the cake are achieved by bringing the charge to the point of onset of fusion and then cooling it for ten to fifteen minutes down to a temperature of 1,300 to 1,325°. Undisintegrated cake is returned to the oven for further sintering, while the disintegrated portion is treated in a solution of soda to obtain a solution of sodium aluminate, which is converted to pure aluminium oxide by normal sintering methods.
30. The spontaneous disintegration of the cake during cooling is caused by the recrystallisation of the beta-modification of the dicalcium silicate formed in the sintering process into a high-volume gamma-modification. In view of the low concentration of Al_2O_3 left in solution after leaching (12-15 grams per litre), the hydrochemical processing of the cake can be so arranged that the operations of silicon removal and evaporation of the residue are entirely eliminated from the technological process.
31. Ferric oxide does not affect the process if the initial material does not contain more than 3 to 5 per cent of it. All that is necessary is to increase the amount of limestone in the charge to a degree that will ensure the formation of dicalcium ferrite. Where there is a higher content of ferric oxide, its detrimental effect on the process can be avoided by adding a reducing agent for it to the charge and sintering in such a way as to ensure that the reducing process takes place in the whole charge.
32. A most important innovation in the development of alumina production from various alumo-silicates by the sintering method is the use of sodium sulphate instead of caustic soda in the process. It will be seen from the bibliography (15) that soda and sulphur can be produced jointly with alumina. Study has also been given to the processing of alunites (16), alumina-rich raw materials such as diaspora-boehmite bauxites (17), and clays and kaolins (18). The same researchers have obtained alumina, soda and cement from more acid nepheline syenites (23).

33. For a number of countries which do not have a domestic caustic soda production industry, the use of sodium sulphate - a raw material that is readily available in nature - facilitates and simplifies the problem of producing alumina from almost any material. Even the preliminary conversion of sodium sulphate into sulphite is not really a complicating factor.

34. It is quite possible that even more important data on the processing of sulphates is available at the Government Mines Branch Research Centre in Canada. This centre has a staff of 635 persons, 256 of whom are university graduates, mainly occupied in the extraction of metals from ores, the selective breakdown of mixtures of metal sulphates, and the design of apparatus for these processes (20)

35. A new development (19) in the production of alumina and soda by sintering the raw materials with the use of sodium sulphite is the 80 to 83 per cent extraction of aluminium oxide and the 95 per cent extraction of alkali from sandstones of the following percentage composition: SiO_2 - 47.48; Al_2O_3 - 20.67; Fe_2O_3 - 8.36; TiO_2 - 0.8; CaO - 0.72; MgO - 0.95; $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ - 6.6; H_2O - 8.2 and other substances - 4.48.

The acid method

36. The acid method of separating alumina is being investigated but it has not as yet found favour in industry for the following reasons:

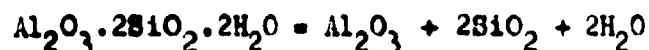
- (a) The corrosive effect of the acids on the materials usually employed for factory equipment. It should be noted, however, that new acid-resistant materials such as pyrocerams and plastics should completely eliminate these earlier difficulties;
- (b) The complications presented by any acid method because of the need to purify the resulting solutions from iron salts;
- (c) The fact that the acid method gives a type of alumina that is less suitable for the production of metallic aluminium by modern (electrolytic) techniques.

37. Nevertheless, acid alumina-production methods may be useful industrially, since they afford greater possibilities, in principle, than alkaline methods for solving the problem of processing high silicon-content materials of the clay and kaolin type, which are available everywhere in large quantities. This is due to the fact that the inertness of silica to acids enables this component of the natural raw material to be taken out of the process in the initial stages without wasting acid reagents.

38. Consequently, the successful development of acid methods should make it possible to widen the range of ores used in the alumina industry by bringing about more extensive industrial use of clays, kaolins and other silicates. This explains the attention that is being paid to acid methods by scientists and technologists, who are striving to overcome the drawbacks mentioned above.

Principal operations in the acid method

39. The principal operations in the acid method are: preliminary treatment of the raw material, breakdown of the raw material by acid, giving a solution of aluminium salts; purifying the aluminium salts of iron compounds; extraction of pure aluminium oxide; and regeneration of the original acid. The preliminary treatment of the raw material comprises crushing, grinding and firing. The purpose of firing is to dehydrate the material to be processed and thus break the chemical bond between its individual elements, thereby increasing the reactivity of the material to any chemical agent, including acids. When kaolin raw materials are broken down by firing, the reaction is as follows:

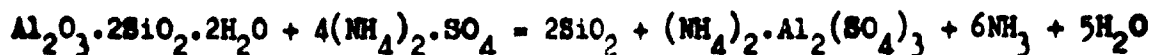


The temperature of disintegration of kaolin is between 560 and 580°C. Overheating of kaolin lowers the reactivity of the separated ingredients, and at a temperature of 950 to 960°C they form a stable compound, sillimanite or mullite ($2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) on which acids have practically no effect whatsoever.

40. The raw material is disintegrated by means of sulphuric, nitric, hydrochloric or sulphurous acid. This produces a solution of aluminium and iron salts. The silicon in the raw material remains in the sediment. Sulphuric acid has long been used to break down raw materials containing alumina for the production of aluminium sulphate.

41. Nitric, hydrochloric and sulphurous acids have the advantage of being comparatively easy to regenerate. Sulphurous acid is also a by-product of a number of metallurgical plants, but to achieve the necessary high concentration of SO_2 , the breakdown process must be carried out under a pressure of several atmospheres in autoclaves.

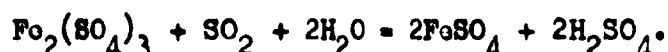
42. Another method is to break down the raw material in a furnace by heating it together with ammonium sulphate:



The ammonia extracted is used in one of the later stages of the process to obtain ammonium sulphate.

43. The elimination of iron compounds can be achieved by a number of methods. One such method, based in the differential solubility of certain aluminium and corresponding iron compounds, enables the aluminium salts to be precipitated out, leaving the iron salts in solution.

44. Thus, for example, in the sulphuric acid method it is possible to make use of the property possessed by aluminium sulphate of forming a double salt with ammonium sulphate. This salt, which is known as ammonium alum, $\text{Al}_2(\text{SO}_4)_3(\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, is easily soluble in hot water but almost insoluble in cold. In view of the fact that ferric sulphate also forms a similar salt with ammonium sulphate, while the lower (ferrous) salt does not interact with ammonium sulphate but remains in solution when it is present, the production of ammonium alum should be preceded by the reduction of the iron compound in solution to the lower (ferrous) form. Either a solution of ammonium bisulphite (NH_4HSO_3) or else sulphur dioxide can be used as a reducing agent, the reaction being as follows:



45. Potash alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, reacts in the same way as ammonium alum to hot and cold water.

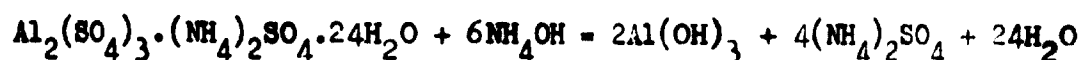
46. As another example it may be noted that, to purify a solution of aluminium chloride, the solution may be saturated with gaseous HCl, which precipitates aluminium chloride hexahydrate, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, while the iron compounds remain almost entirely in solution. Another method worthy of attention is based on the use of certain surface-active substances, such as manganese dioxide (MnO_2), which are capable of absorbing (adsorbing) the iron compounds on their surface and thus taking them out of solution. This last method, which is connected with the new and rapidly developing branch of science known as physico-chemical mechanics, should be especially borne in mind both for the above-mentioned use and for the investigation of other likely possibilities in the technology of enriching the raw and partially processed materials for aluminium production. Pure aluminium oxide is extracted by calcining such of the compounds containing it as are :

decomposable by heat. As well as aluminium oxide, calcination produces the corresponding acid oxides and, in the case of aluminium chloride (which is calcined in the presence of steam), gaseous hydrogen chloride also.

47. When potash alum is fired with aluminium oxide, potassium sulphate is also obtained. The fired product is therefore washed, the resulting solution evaporated, and the potassium sulphate extracted from it. Part of this potassium sulphate can be disposed of commercially (as, for example, when processing alunite raw material), while part is used as a feedback product in the earlier stages of the process.

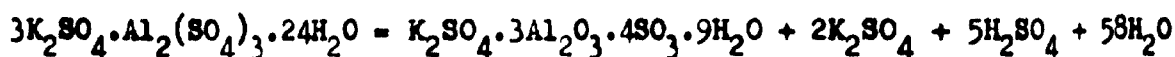
48. Although most aluminium salts break down completely at comparatively low temperatures (200-400°C) and only aluminium sulphate requires higher temperatures (770° and over), in practice, in the case of purely acid methods, the calcination of aluminium salts must end with the normal temperature for the calcination of alumina, which is in the region of 1200°C. This is necessary in order to fully remove the acid residue from the aluminium salts and to ensure that the aluminium oxide is not hygroscopic. The firing operations are carried out in rotary furnaces, in multi-hearth furnaces with mechanical super heating from hearth to hearth, or in a fluidized bed furnace.

49. The breakdown of the ammonium alum can also be done chemically by processing with ammonia according to the formula:



50. The residue of the aluminium hydroxide is separated from the solution and washed and fired as usual. The ammonium sulphate, on the other hand, is a feedback product and is used, as was mentioned above, in the earlier stages of the process, although in some methods the ammonium sulphate is also a commercial product, sold for use as fertilizer.

51. The firing of aluminium salts which crystallize with the liberation of a large amount of water, such as potash alum, presents clear technical difficulties, owing to the ease with which such salts, even at low temperatures, melt in their own water of crystallisation. In such cases, in addition to firing in a fluidised bed furnace, recourse may be had to a special procedure based on the observation that when the alum solution is heated in autoclaves to a temperature of about 200°C, the alum breaks down according to the reaction:



The so-called basic alum which is thus precipitated is finally dehydrated by the usual method, and the above-mentioned complications do not arise.

52. The sulphuric acid obtained by the above reaction is a feedback product and is used for breaking down new batches of minerals. The acid is regenerated, in the case of nitric, sulphurous and hydrochloric acids, by simple absorption by water of the volatile products of calcination, or in the case of sulphuric acid by more complex special chemical processing. Sometimes, as may be seen from the above formula for the breakdown of potash alum in an autoclave, one product of the decomposition of aluminium salts is the original acid, which for further use only requires boiling down and regenerating.

53. The Canadian aluminium industry is already producing alumina from clays and shales, and five technological plans for this process have been published (21). The raw material is crushed and ground, leached with sulphuric acid, and the silica, titanium and iron compounds, and other impurities are filtered off, after which the aluminium sulphate solution is cooled, causing the aluminium sulphate to crystallize out. The aluminium sulphate is then centrifuged out of the mother liquor, which is returned to the raw material acid leaching stage. The journal article referred to also reviews the economics of the process.

54. An account of what appears to be the same process is published in another source (22), where reference is made to a method developed in 1961 for the chemical processing of clay and shale into high-quality alumina by the Olin Mathieson method. In the method described, the raw material is leached with sulphuric acid, the iron and the aluminium sulphate are separated by crystallisation and the aluminium sulphate thus obtained is broken down thermally.

55. In the method developed by the Anaconda firm, the raw material is treated with hydrochloric acid, the resultant aluminium chloride and iron are concentrated by evaporation, the $AlCl_3$ is broken down thermally, and the iron is removed by heating with NaOH or by sintering with sodium carbonate (soda).

56. It is possible that tomorrow's alumina and aluminium technology will also make use of the very interesting French studies of acid soils (24), in which appreciable quantities of free aluminium, not forming part of the crystal lattice of the argillaceous minerals of the soil, were observed. It is conjectured

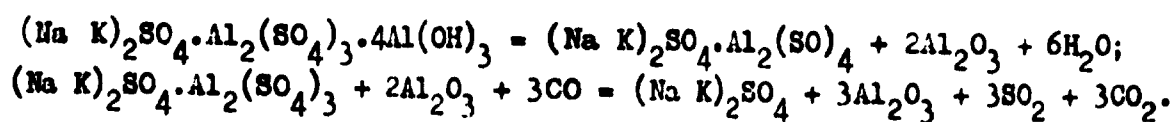
that the aluminium is present in the form of an exchange-ion. Similar studies of soils in Poland (25), in which 2,800 samples taken from an area of 4,500 hectares in the Oder valley were analyzed, showed free aluminium in 667 samples in a quantity of more than 5 mg per 100 g of soil, the conclusion being that at least 20 per cent of the soil contained exchange-ion aluminium.

57. In Poland, too, aluminium sulphate is produced from clay with a low aluminium oxide content by treating the clay with sulphuric acid and calcining in rotary kilns. Relatively pure aluminium sulphate is leached out of the cake thus obtained (26). Research into the production of aluminium sulphate from clays is also being carried out in Egypt (27).

The production of alumina from alunite

58. Recent research into the technology of alunite processing has led to the introduction of reduction heating as a separate step from the firing operation and has confirmed the expediency of treating calcined alunite by the combined ammonium-alkaline method.

59. In this new process, the alunite is ground, after which it is fired and reduction heating takes place in fluidized bed furnaces. The reaction that takes place is as follows:



60. A theoretical basis for the selection of the optimum firing temperature is provided by the curve for the heating of alunite. This curve shows that the thermal stoppage of dehydration occurs in the temperature range 500 to 520°C, which is also the optimum temperature for firing. At lower temperatures, dehydration is only partial, while higher temperatures lessen the reactivity of the gamma-oxide of aluminium present in dehydrated alunite. For these reasons, the reduction of alunite is carried out at temperatures not exceeding 540°C.

61. As a result of the separate firing and reduction of alunite, sulphur dioxide is obtained in a concentrated state (up to 75 per cent by volume) and can conveniently be used for the production of sulphuric acid. Because the alunite is processed at low temperatures, the alumina obtained dissolves readily in caustic soda solutions of relatively low concentration (110-120 g per litre) at

temperatures not requiring the use of autoclaves. The aluminate solution obtained through leaching, which contains approximately 100 g of Al_2O_3 per litre, has a caustic module of 1.8-1.9 and an SO_3 content of 30 to 40 g per litre, is separated from the mud and converted into alumina by means of the apparatus and technology normally employed in the Bayer process.

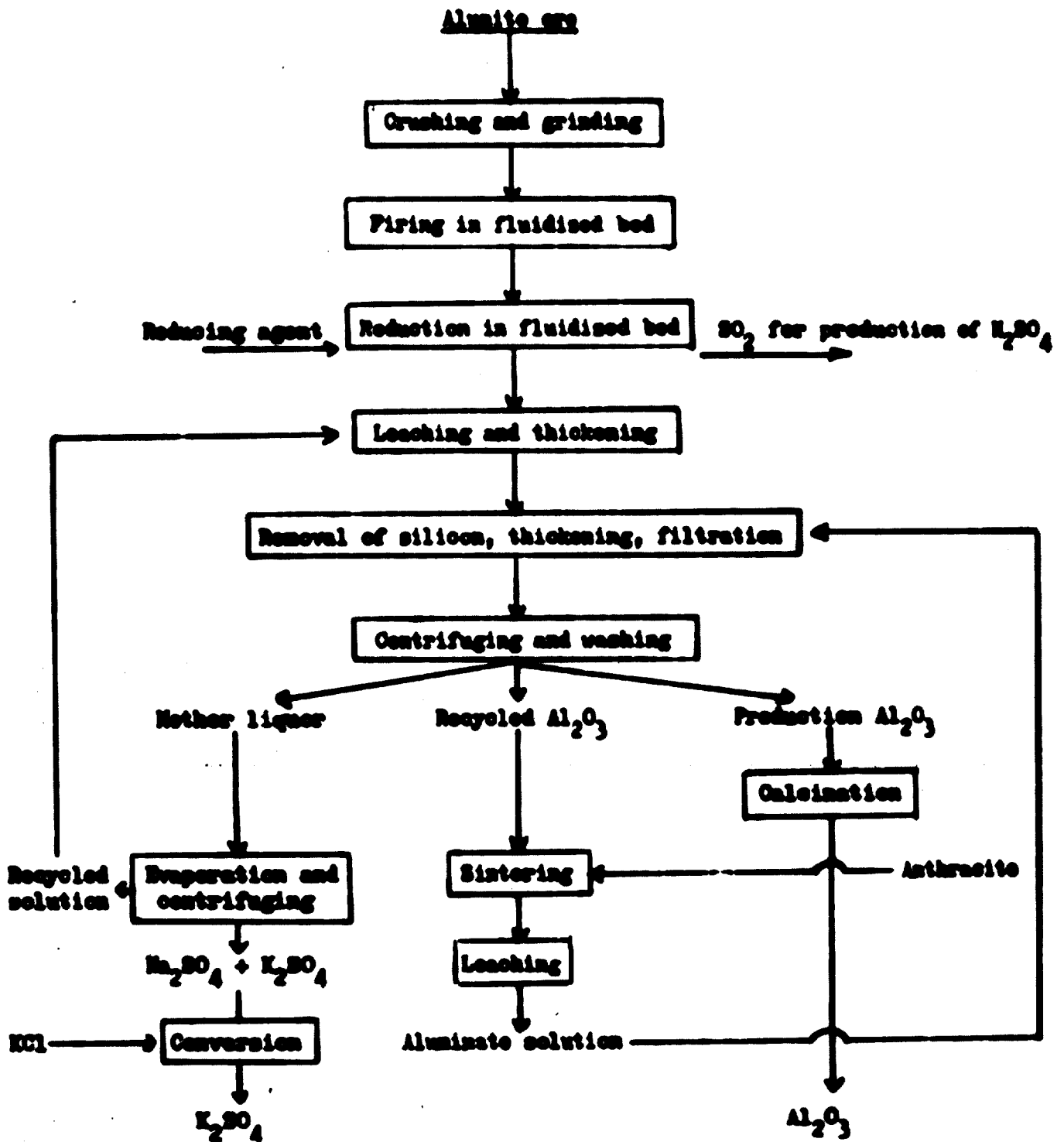
62. The only distinctive feature of the method just described is that the aluminate solution obtained, the silicon modulus of which does not exceed 130, must go through an operation for the removal of silicon. This is done at a temperature of 103 to 105°C, by mixing the aluminate solution with seed sodium aluminosilicate obtained in preceding silicon-removal operations.

63. The recirculated solution is evaporated, thus separating out the potassium and sodium sulphates. Since, in the reduction firing process, up to about 15 per cent of the aluminium sulphate contained in the alunite remains undecomposed, an equivalent quantity of caustic alkali is converted in the leaching process into an alkali sulphate, while some more of the caustic alkali originally introduced into the process is used up in the formation of alkali aluminosilicate in the leaching and silicon removal processes. To compensate for these losses, part of the sulphate separated out in the evaporation of the recycled solution is converted into caustic alkali in a secondary branch of the process by sintering it with aluminium hydroxide in the presence of a reducing agent. The remainder of the potassium sulphate/sodium sulphate mixture, which is available for commercial disposal, is converted into the more valuable potassium sulphate, for which purpose it is treated with potassium chloride solution.

64. In the processing of alunite rock containing about 50 per cent alunite (the rest being quartz), 6.66 tons of ore, 710 m³ of producer gas (1450 kcal/m³), and around 7 tons of steam are needed to produce 1 ton of aluminium oxide. The by-products obtained are sufficient sulphur dioxide for the production of 1.26 tons of sulphuric acid monohydrate and 0.235 tons of potassium sulphate, plus 0.14 tons of KCl. A flowsheet of the reduction method of producing alumina from alunite is given in table 6. (2) (3)

65. A new type of alumina-containing raw material is natural sulphates of aluminium, which occur in two forms: in combination with magnesium $\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ (pickeringite) and as alunogen $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$. In the deposits referred

Table 6
General technological diagram of the reduction method
for the production of alumina from aluminite



to below, these materials are accompanied by opocnite, $MgSO_4 \cdot 7H_2O$, certain amounts of sulphates of iron and nickel, and by limonite.

66. The deposits of these materials which have been explored in the Argentine province of San Juan near the town of Calingasta contain reserves of approximately twelve million tons. A deposit of pickeringite is also known to exist in Salta province but its extent has not been explored. The deposits of pickeringite in the neighbouring republic of Chile are believed to be even larger.

67. The average chemical composition of the sulphates in the deposits that have so far been explored, according to the findings of geologist Natalia Rossi, are as follows: $Al_2(SO_4)_3$ - 20.75%; $MgSO_4$ - 10.66%; $Fe_2(SO_4)_3$ - 6.74%; $FeSO_4$ - 3.12%; remainder: water. The average content of anhydrous SO_3 is 12 per cent, while the ratio of useful oxides $Al_2O_3:MgO$ = 4.5. In the opinion of several Argentine geologists, more extensive exploration of the mountainous regions bordering upon the areas referred to might well reveal further deposits of the sulphates mentioned above.

68. The theoretical composition of natural pickeringite is as follows: $Al_2(SO_4)_3$ - 39.8%; $MgSO_4$ - 13.9%; and H_2O - 46.2%, giving, in the anhydrous state, an aluminium sulphate content of 74.1 per cent and a magnesium sulphate content of 25.9 per cent. This would correspond to an aluminium oxide content of about 12 per cent in the natural state and 22 per cent in the anhydrous state.

Technical considerations on the method of obtaining alumina from pickeringite

69. Up to the present time, practical investigations on the treatment of pickeringite have either not been carried out or else their results have not been published. It is only possible to speak of the methods of treatment of pickeringite in a general manner. It is well known that pickeringite, alunogen and other sulphates found in rock are easily soluble in water. It seems reasonable therefore to assume that they could be freed of possible accompanying impurities that are not soluble in water by centrifuging an aqueous solution.

70. After treating the solution thus obtained with ammonia by the method described above, ammonium alum compounds of aluminium are obtained which are soluble with difficulty in cold water; these too are separated by centrifuging. It is well known that magnesium sulphate does not form difficult soluble compounds

with ammonia, and the same applies to the other ingredients, except for ferric iron which must therefore be transformed into the lower ferrous form as a preliminary step.

71. The natural mineral boussingaultite $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ is soluble in water, while the other natural mineral morenosite $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and the form of morenosite in combination with magnesium (pyromelin) are readily soluble in water. In addition to the methods considered above for separating the sulphate components of pickeringite, these components can also be separated by using differential heat treatment and breakdown in an oxidising medium:

	<u>$\text{Al}_2(\text{SO}_4)_3$</u>	<u>MgSO_4</u>
Heat of formation, kcal/mole	820.98	305.5
Temperature of decomposition in an oxidising medium	770°C	1100-1200°C

72. There may also be other methods of solving the problems of breaking down the sulphate components of pickeringite which have been worked out in practice but not yet published. The most reasonable thing to do, in this connexion, would be to turn first of all to the work of the Canadian Government Mines Bureau Research Centre, which specializes in the breakdown of metal sulphates.

73. The practical solution of this question must undoubtedly be preceded by a fully laboratory investigation of the details of the technological process and a test of the process in a half-scale pilot plant; this would be extremely useful for countries possessing deposits of pickeringite, as it would enable them to use the extremely valuable components making up this material.

III. GENERAL CONCLUSIONS

74. The solution to the problem of providing raw materials for the future production of alumina must be sought basically in the comprehensive processing of the great rock matrices which are the sources of the present raw materials for alumina production: namely, bauxites and laterites.

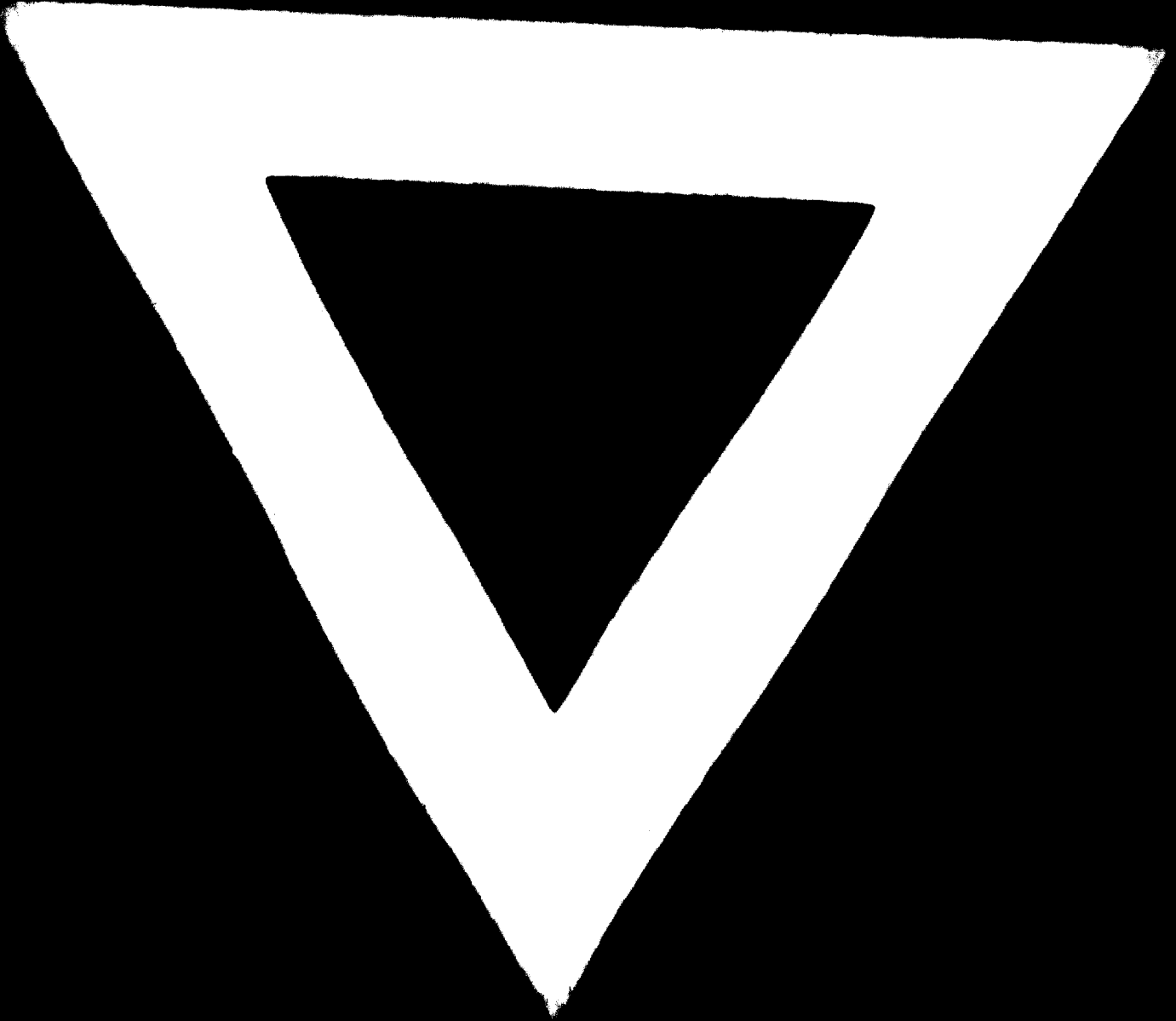
75. Naturally, an effective method must first of all be worked out for the processing of laterites and mountain rock deposits that have begun the process of weathering and which contain either high concentrations of aluminium oxide or large contents of other components suitable for comprehensive extraction.

76. The separation of the alumina and other useful components is facilitated by finely dispersing the ores and the iron-reducing agent, using the most active type of peat and coal of vegetable origin (the consumption of these is only half that of coke and they are quickly restored by nature), and bringing the reduced iron into a finely-dispersed state in which it is easily removed by electro-magnetic separation.
77. The quickest and most effective solution of this whole problem can only be reached under the auspices and through the resources and effort of the Metallurgical Industries Section of the United Nations.
78. The processing of aluminium silicates into alumina becomes industrially feasible when there is the right combination of economic factors such as the availability of cheap raw materials, cheap power and cheap chemical reagents (e.g. sodium sulphate), the generation of SO_2 as a by-product, or the production of surplus chlorine, when aluminium silicates can be treated by chlorination (silicones and similar compounds).
79. The utilisation of sulphate raw material such as pickeringite and alunite may in the near future satisfy the local needs of countries that have such raw material at small expense.
80. For the future production of alumina, it would be best to concentrate on the processes described in references (7) and (31).

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